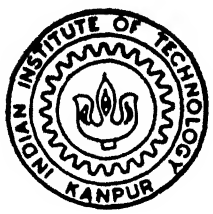
CLEAVAGE OF COBALT–CARBON BOND IN ORGANOCOBALOXIMES AND ORGANODICOBALOXIMES : HOMOLYTIC AND HETEROLYTIC PATHWAYS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by

VANDANA DIXIT



to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

August, 1993

Dedicated
to
the Divine feet of
Sri Santosh K Dwivedi
&
my parents

STATEMENT

I hereby declare that the matter embodied in this thesis "Cleavage of Co-C Bond in Organocobaloximes and Organo-dicobaloximes : Homolytic and Heterolytic Pathways" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor B.D. Gupta.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators, The author is responsible for purely unintentional oversights and errors which could be traced herein.

Vdixit 18.8.93

Vandana Dixit

Kanpur
August 16, 1993

CERTIFICATE

Certified that the work "Cleavage of Co-C Bond in Organocobaloximes and Organodicobaloximes : Homolytic and Heterolytic Pathways" presented in this thesis, has been carried out by Ms. Vandana Dixit, under my supervision and the same has not been submitted elsewhere for a degree.

(B.D. GUPTA)
Thesis Supervisor
(Professor)
Dept. of Chemistry
I.I.T.-KANPUR

Kanpur
August 16,1993

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Ms. Vandana Dixit has satisfactorily completed all the course requirements for Ph.D. degree programme in Chemistry. The course include :

CHM 602	ADVANCED ORGANIC CHEMISTRY
CHM 605	PRINCIPLES OF ORGANIC CHEMISTRY
CHM 624	MODERN PHYSICAL METHODS IN CHEMISTRY
CHM 625	PRINCIPLES OF PHYSICAL CHEMISTRY
CHM 645	PRINCIPLES OF INORGANIC CHEMISTRY
CHM 646	BIO INORGANIC CHEMISTRY
CHM 681	BASIC BIOLOGICAL CHEMISTRY
CHM 800	GENERAL SEMINAR
CHM 801	SPECIAL SEMINAR
CHM 900	POST GRADUATE RESEARCH

Ms. Vandana Dixit has successfully completed her Ph.D. written and oral qualifying examinations and was admitted to the candidacy of Ph.D. degree in March, 1990.

(P.K. Ghosh)
Professor and Head
Department of Chemistry
I.I.T. KANPUR

(Y.D. Vankar)
Convener
Departmental Post-Graduate
Committee, Department of
Chemistry, I.I.T. KANPUR

SYNOPSIS

In recent years the physical and chemical studies on organocobaloximes[*1] appear to focus on their chemistry as more of an independent area rather than as model for vitamin B_{12} chemistry. Furthermore, with the recent information that cobaloximes can be used as potential industrial catalysts and synthetic inorganic mediators in carrying out a number of interesting and useful chemical transformations a new field of research is emerging.

Organocobaloxime chemistry, therefore, becomes one such area which offers promising features to become a useful synthetic route to many new and novel organic systems. The thesis entitled "Cleavage of Co-C bond in Organocobaloximes and Organodicobaloximes : Homolytic and Heterolytic Pathways", deals with the organometallic aspects of organocobaloxime chemistry. The work has been divided in four chapters.

The first chapter describes a comprehensive and detailed account of the literature survey on the organocobaloxime chemistry. A special emphasis is made on the stability of Co-C bond, various synthetic methodologies for the preparation of organocobaloximes and their reactions with electrophilic and free radical precursor.

It is quite well established that Co-C bond in organocobaloximes is weak and its cleavage may be induced in many ways including electrophilic, nucleophilic and free radical attack at the R group. Besides, oxidation/reduction of RCo(III) and the modifications within the R group also effect the Co-C bond cleavage. Since organocobaloximes show susceptibility towards

electrophilic displacement reactions and indeed to oxidation by some of the same electrophiles, a direct heterolytic cleavage of the Co-C bond may compete with the homolytic pathway. This is particularly found in the reactions at a saturated carbon centre in organocobaloximes with electrophilic free radicals. The problem of mixed mechanism is further aggravated by the fact that organocobaloximes are prone to homolysis and frequently contain traces of cobaloxime(II) which can initiate a chain process even when the heterolytic pathway might otherwise be dominant.

A good deal of work has been done on the chemistry of arene sulphenyl halides and it is known that depending upon the nature of reagent and the reaction conditions, these reagents have a high affinity for both ionic as well as free radical reactions.

Chapter 2 describes the reactions of benzene sulphenyl chloride (A), pentachlorobenzene sulphenyl chloride (B) and 2,4 dinitrobenzene sulphenyl chloride (C) with various organocobaloximes under thermal and photochemical conditions. This chapter is subdivided into 2A and 2B. The subsection 2A describes the synthesis of organic precursors and the synthesis of organocobaloximes. In all, 31 organocobaloximes including alkyl, benzyl, allyl and heteroaromatic methyl cobaloximes have been synthesized. The subsection 2B describes the reactions of arene sulphenyl chlorides with the organocobaloximes. Alkyl and benzyl cobaloximes react with (A), (B) or (C) under thermal and photochemical conditions to give the corresponding organic sulphides in 50-85% yield. However, in the reaction of benzyl cobaloximes with (C) additional products like the bibenzyl and the benzyl ethers of dimethylglyoxime are also formed in each

The reactions of arene sulphenyl chloride (A, B and C) with furfuryl, 2- and 3-thienylmethyl cobaloximes are in general complicated and a mixture of products, both organic and organometallic, are formed in each reaction. The detailed study shows that the reaction condition, the nature of the substrate cobaloxime and the arene sulphenyl chloride, all seem to effect the product distribution. These organocobaloximes form a unique class of organometallic compounds where both the aromatic ring as well as the Co-C bond are simultaneously activated towards the attack of the electrophile. A suitable mechanism is proposed for the formation of all the products.

The reactions of allyl cobaloximes with (A), (B) and (C) are also dealt in this chapter. Allyl, 3-methyl allyl, 3-phenyl allyl and 3,3-dimethyl allyl cobaloximes form the corresponding regiospecifically rearranged sulphides as the exclusive organic products. α-Pinenyl cobaloxime forms different products with each of the three reagents. Interestingly, the sulphide formed from the reaction with (B) rearranges on the column with the opening of the cyclobutane ring. The reactions follow a free radical pathway with the $\dot{S}Ph$ radical attacking on either the α or γ carbon of the allyl group with a simultaneous displacement of the Co(II) species.

As organocobaloximes are prone to reactions with both electrophilic and free radical reagents, in most cases especially where the reagent is not particularly electrohilic or where the electrophilic centre is different from the reactive site of the free radical, the distinction between the two mechanisms may readily be established. However, when the reagent is symmetrical,

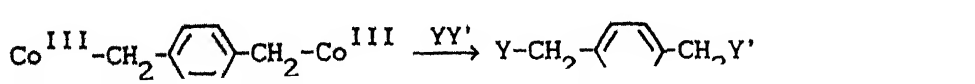
even through nucleophilic species may lead to identical products, the mechanism is difficult to establish. Nevertheless, such reactions may still provide useful synthetic processes.

Thiocyanogen, a pseudohalogen, shows interesting chemistry as it has two reactive centres and it is known to undergo both electrophilic and free radical reactions.

The chapter 3 describes the reaction of organocobaloximes with thiocyanogen at ambient temperature. n-Butyl and benzyl cobaloximes on reaction with thiocyanogen form the corresponding thiocyanates as the exclusive organic products. 3-But 3-enyl cobaloximes form both cyclic as well as acyclic thiocyanates whereas 5-methyl hex 5-enyl forms the acyclic thiocyanate. The allyl cobaloximes form a mixture of 1,1 disubstituted allyl thiocyanates and isothiocyanates. The low temperature study reveals that the 1,1 disubstituted allyl isothiocyanate arises as a result of the rearrangement of the intermediate 3,3 disubstituted thiocyanate. The results are interpreted in terms of a free radical mechanism.

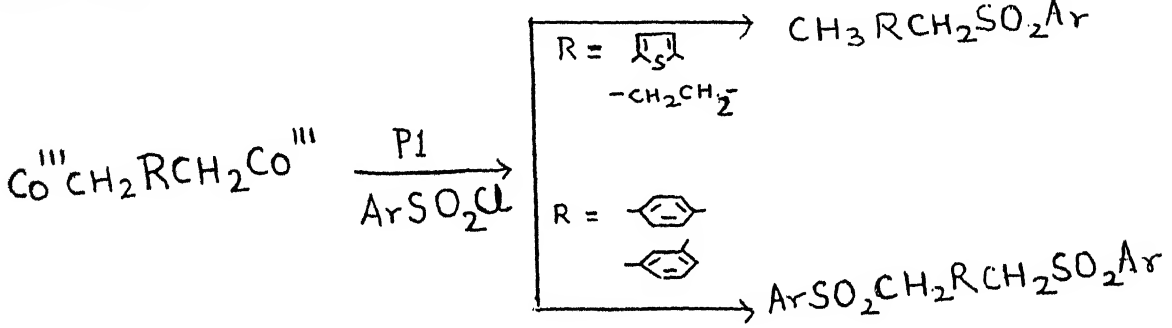
Chapter 4 describes the synthesis of organodicobaloximes and their reactions with arene sulphonyl chloride under thermal and photochemical conditions. The recent work on the reactions of organocobaloximes with free radical precursors have clearly shown that the organic group can be easily functionalised by the C, S or N centred radicals.

In principle, organocobaloximes having two Co-C centres can be similarly functionalised by two similar or dissimilar groups.



Y may or may not be similar to Y'

Four organodicobaloximes are synthesized and their reactions with arenesulphonyl chloride under thermal and photochemical conditions have been done. Meta and para-xylenene dicobaloximes form the corresponding disulphones whereas bis (2,5 thienyl methyl) dicobaloxime and 1,4 butane dicobaloxime form the corresponding methyl substituted monosulphones under all conditions.



Only very preliminary work has been done and the results obtained are significant and are interpreted in terms of S_H2 and electron transfer processes.

Finally a summary of the results of the conclusion and scope for the future investigation is presented.

LIST OF PUBLICATION

1. SO_2 insertion into organocobaloximes : a true insertion or a case of radical chain process?

   B.D. Gupta, Maheswar Roy, Moni Oberoi and Vandana Dixit

   J. Organometal. Chem., 430 (1992) 197-204.

2. Homolytic displacement at saturated Carbon : Part 5. Synthesis of cyclopropyl methyl, Bicyclo [3.1.0] hept-2-yl, Bicyclo [4.1.0] hept-2-yl and cyclohexene spirocycloprop-2-yl sulfones from the corresponding But 3-enyl cobaloximes.

   B.D. Gupta, Indira Das and Vandana Dixit

   J. Chem. Res. (S), 1992, 306-307, (M), 1992, 2409-2446.

3. Homolytic Displacement at saturated carbon in organocobaloximes : Part 6. Synthesis of benzyl sulphones.

   B.D. Gupta, Indira Das and Vandana Dixit

   Ind. J. Of Chem. (in press).

4. Homolytic displacement at Saturated carbon : Part 7. Synthesis of cyclic, bicyclic and spirocyclic sulphones from the corresponding Butenyl cobaloximes with thiophene-2-sulphonyl chloride.

   B.D. Gupta, Indira Das and Vandana Dixit

   Ind. J. Chem. (in press).

5. Cleavage of Co-C bond in Organocobaloximes : Reactions of allyl cobaloximes with arene sulphenyl chloride : Part 8.

   B.D. Gupta, Vandana Dixit and Indira Das

   Inorg. Chim. Acta (submitted).

6. Homolytic displacement at saturated Carbon in organodicobaloximes.

   B.D. Gupta and Vandana Dixit

Publications (contd.)

Seventh European Symposium on Organometallic Chemistry, Namur, Belgium, July 15-19, 1991.

7. Co-C bond cleavage in the reactions of alkyl, benzyl, and heteroaromatic methyl cobaloximes with arene sulphenyl chloride : Homolytic and Heterolytic pathways.

   B.D. Gupta and Vandana Dixit (manuscript under preparation).

8. Reactions of thiocyanogen with organocobaloximes : Novel synthesis of allyl and cyclopropyl carbinyl thiocyanates.

   B.D. Gupta, Vandana Dixit and M.D. Johnson (manuscript under preparation).

* Part contribution but not included in the thesis work.

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Vandana Dixit

CONTENTS

CHAPTER - 1

ORGANOCOBALOXIMES : POTENTIAL ORGANOMETALIC SYNTHETIC PRECURSORS

CHAPTER - 1

Organometallic chemistry, an interdisciplinary science has grown at a phenomenal pace during the last 3-4 decades. The history of organometallic chemistry may be described as one of the unexpected discoveries. Organometallic chemistry is the borderline area between the classical subdivision of organic and inorganic chemistry. It thus covers a) the compounds in which metal and carbon are linked by a sigma bond, b) metal carbonyls and their derivatives and c) compounds in which unsaturated organic molecules are bonded to metals through Pi bonds.

The beginning of the chemistry of sigma bonded organometallic compounds dates back to 1760 when tetramethyldiarsine was isolated as a byproduct in the photolysis of cobalt ore smaltite[1]. It took almost one hundred years to characterize the compound[2]. Frankland in 1849 isolated and characterized diethyl zinc - the first ever organometallic compound with metal to carbon bond[3]. On the other hand, the first olefin-metal compound, the Zeise's salt was reported in 1927[4,5]. Since then a tremendous effort has been made to synthesize and study a large number of organometallic compounds. The names of Grignard, Gilman, Ziegler, Wilkinson and many others are noteworthy for their significant contribution to organometallic chemistry. Their work has been periodically reviewed in the literature[6-15].

1.1 Co-C Sigma bond : A poor knowledge

The chemistry of organocobalt complexes was limited to a group of ill-defined alkyl and aryl compounds until 1950[16]. However, with the great expansion in organometallic chemistry in

late 1950's and aided by the knowledge that C-Transition metal bond might be stabilised by certain ligands, there was also some progress into the synthesis of organocobalt complexes[17]. Dialkyl cobalt, used commercially as an additive in drying oils, may be the first stable complex of cobalt[18]. Later on, the organocobalt complexes with the empirical formula $RCoX_n$ (R = α,β naphthyl, X = Br,I) were prepared but partially characterized[19]. A few acetylide complexes[20] and aryl complexes[21] (partially or fully characterized) have also been reported[22,23].

By the late 1950's it has become very obvious that the sigma bonded organometallic compounds of main group elements and transition metals contribute a diverse and rich field of research. However, the chemistry of Co-C sigma bond could not be enlightened to a similar degree even by the middle of this century.

1.2 Mother Nature : Beginning of a new era

At a time when sigma bonded organocobalt chemistry was passing through a dormant phase, there came one of the most interesting developments that have occurred so far in organometallic chemistry. This was the isolation of vitamin B_{12} coenzyme by Barker[28] in 1958 and the subsequent discovery by Lenhert and Hodgkin[24] that it contained an adenosyl group linked to cobalt by a direct Co-C sigma bond indicated for the first time the occurrence of organometallic reactions in biological systems. This was considered to be one of the most stable sigma bonded organocobalt compound ever reported. The contemporary chemical studies showed that this bond was uneffected by a number of reagents which cleaved bonds elsewhere in the molecule[25]. While

vitamin B_{12} coenzyme and methylcobalamin were recognized to play important and distinctive biochemical roles, they were not accessible in quantity for studies under nonenzymatic conditions.

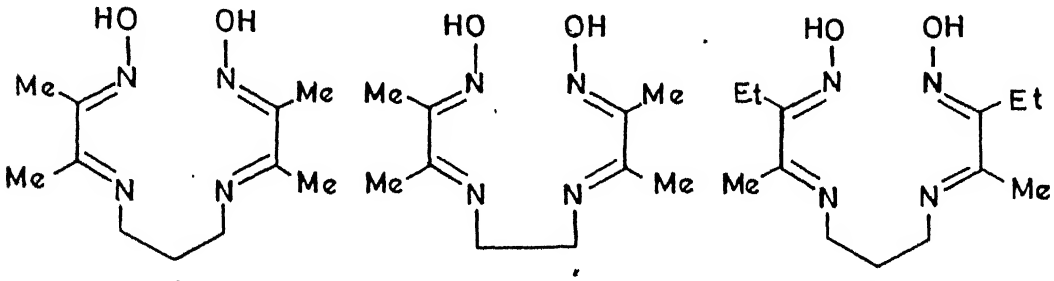
The realisation of the fact that vitamin B_{12} coenzyme formally a Co(III) complex, and this corrin ring might be an important factor in the stabilization of Co-C bond, stimulated the search for simpler models, complexes that contain a stable Co-C bond axial to a planar equatorial ligands, which could simulate the reactions of the cobalt atom in this complicated corrin. These ideas[26,27] led to the synthesis of a large number of sigma bonded organocobalt complexes.

1.3 Co-C sigma bond : Synthesis begins

The discovery of the vitamin B_{12}-like chemical properties of complexes of bis(dimethylglyoximate) cobalt i.e., the cobaloximes by Schrauzer and Kohnle[29] in 1964 demonstrated the feasibility of the above approach and in turn stimulated the search for other models. It was soon established that the stability of Co-C bond virtually depended upon the optimally strong, essentially planar ligand field. Moreover, the coordinating atoms of the equatorial ligand do not have to be necessarily nitrogen but may be substituted partially by oxygen. Subsequently, numerous other cobalt-chelates were tested as possible vitamin B_{12} models, notably the propylene and ethylenediimmine complexes of diacetylmonoximes, and Schiff bases derived from salicylaldehyde and acetylacetone, particularly by Costa and his coworkers[30].

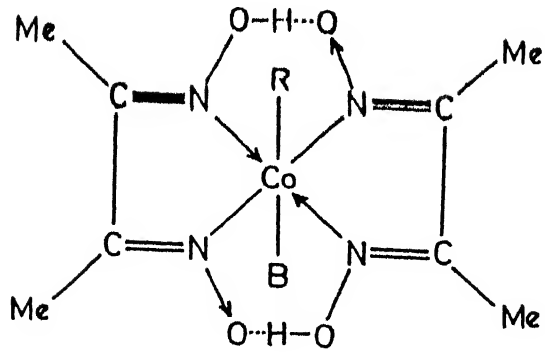
Among the models reported thus far, Costa's cobalt chelates of 1[31], its ethylenediimmine analogue 2[31b,32], and the related

ligand 3[33] are the only monoanionic ligands like the naturally occurring corrin. However, although 1 was shown by electrochemical measurements to exhibit oxidation-reduction potentials closely resembling those of vitamin B_{12}[34], Schrauzer



warned[35,64] that it is not a bonafide vitamin B_{12} model because, in contrast to vitamin B_{12}, on reductive alkylation it is easily overreduced, giving rise to neutral dialkyl derivatives, first described by Costa and coworkers[36]. The cobalt complex of ligand 2, on the other hand, cannot be readily reduced to Co(I) form under conditions applicable to vitamin B_{12} or to the cobaloximes. According to Schrauzer et al[32], this is due to their higher Co(II)/Co(I) reduction potential, reduction to the Co(I) derivatives was possible in nonaqueous solvents such as diglyme and pyridine, with sodium amalgam as reductant. As small structural changes have profound effect on the reactivity of the cobalt atom, other models have also been considered[37]. Today, a wide variety of equatorial ligand systems are known that ranges from aromatic porphyrins[38] to the completely saturated [14] ane N_4 systems[39] with more than two thousand five hundred organocobalt complexes in the literature. However, it must be emphasized that because of their close similarity of chemical properties to vitamin B_{12} coenzyme, cobaloximes (fig. 1) are the most studied

ones[40] and I have preferred to use these systems in my thesis studies.



Organocobaloxime

Fig. 1 Reproduced from ref. 43.

Before I describe the general methods of synthesis of organocobaloximes, it is worthwhile to discuss factors which stabilise the Co-C bond.

1.4 Stability of Co-C bond

Alkyl cobaloximes and alkyl cobalamins are thermally stable compounds. One possible way of expressing this axial Co-C bond stability may be through the resonating structure as follows[41,42]

$$\begin{array}{ccccc} R & & R^- & & R^+ \\ | & & | & & | \\ (Co) & \longleftrightarrow & (Co^+) & \longleftrightarrow & (Co^-) \\ | & & | & & | \\ B & & B & & B \end{array}$$

A knowledge of the Co-C bond character has been derived from the changes in the orbital energies on the formation of the bond between a $d^7(Co^{II})$ species and the organic radical. The d-orbital arrangement of the former has been considered to be intermediate

between that for the d^8 system, in which the d_{xy} orbital is believed to be appreciably higher in energy than the d_z^2, and the d^6 system in which the energy of $d_z^2 > d_{xy}$ orbital. As the bond formation involves the pairing of the d_z^2 orbital with the carbon sp^3 orbital, the stability of Co-C bond will depend upon the relative stability of these two orbitals and upon the relative energies of the d_{xy} and d_z^2 orbitals.[43] LCAO-MO calculations further indicate that the interaction of $3d_z^2$, $4p_z$ and 4s orbitals of cobalt with the carbon sp^3 orbital is mainly responsible for the Co-C bond stabilisation[44]. If the organic residue (R) is sp^2 or sp hybridised carbon, then, additional interactions of the π carbon orbital with $3d_{xz}$ and $3d_{yz}$ orbitals of cobalt lead to further stabilisation of the Co-C bond[43]. Besides, any changes in the second axial base ligand profoundly affects the stability of the Co-C bond trans to it (Trans influence). Thus, more basic ligands have been shown to stabilise the organocobalt(III) complexes further. In addition, the equatorial ligands also affect (Cis-influence) the Co-C bond stability, however, this effect is much less pronounced than the trans influence.

In a variety of experiments on alkyl cobalamins and their models it has always been felt that steric factors (of R as well as the equatorial ligand framework around the Co^{III} centre) play a significant role in the energetics of the metal-carbon bond[43-45]. Recent, theoretical calculations on model compounds also support this view[46]. An interesting linear relationship between Co-C bond length and the number of substituents on the α carbon to cobalt has been observed in the X-ray data analysis[45]. It has been suggested that the weakening of the Co-C bond is triggered by

steric perturbations involving conformational distortion of the corrin ring towards 5'-deoxyadenosyl group[47].

Recently, Datta and Sharma[48] have successfully used multi regression analysis using Taft's polar substitutent constants (σ^*) and Dubois parameter (E'_s,) to explain the properties of alkyl cobaloximes (R = alkyl) and alkyl cobalamins related to the effects of R groups. They have studied the properties like redox potential of the Co^{III}-Co^{IV} couple, Co⟶C charge transfer analysis, trans influence and trans effect of R in alkyl cobaloximes/cobalamins. The study concludes that the Co^{III}-R bond strength decreases with decrease in ($\sigma^*+\lambda E'_s$,) where λ is the mixing coefficient. The steric demand of the corrin moiety is found to be one order of magnitude higher than that of dimethylglyoximate. Similar successful[49] and unsuccessful[50-51] attempts have also been reported in the literature.

The Co-C bond dissociation energies (BDE) of a number of organocobalt(III) complexes and coenzyme B_{12} have recently been estimated independently by Halpern et al[43,47,52] and Finke et al.[53] The latter in a more exhaustive fashion reported reaction products, kinetic parameters, ΔH^*, ΔS^*, and Co-C bond dissociation energies. They have also reported the pH dependent bond cleavage of Co-C bond (heterolysis at pH ≈ 4, 80%, homolysis at pH ≈ 7, 90%). Halpern's group, on the other hand, calculated the BDE for Adocbl assuming only homolytic cleavage and obtained a value of ≈ 30±2 K cal mol^{-1} whereas Finke's value is about 26 K cal mol^{-1}. BDE's for organocobaloximes range between 17-25 K cal mol^{-1} [52].

1.5 Compounds of Co(III) : General methods of synthesis

The preparation of organocobalt(III) complexes has offered interesting and useful reactions in organometallic chemistry. These complexes have been prepared by a large number of ways and have enriched the organometallic chemistry and paved way to the synthesis of various other organometallic compounds. The methods have been adequately reviewed from time to time[54-63].

In general, four main methods have been used for the formation of Co(III)-C bond. These are the reactions of

A. $(Co^{I})^{-}$ or (Co)-H species with electrophilic reagents (e.g., MeI, alkene or alkyne),

B. (Co^{II}) complexes with radicals

C. (Co^{III}) complexes with nucleophilic reagents (e.g., Grignard or organo lithium) reagents, and

D. modification of the organic group.

A. Preparation from $(Co^{I})^{-}$ complexes[54-64] :

The most versatile route to organocobalt(III) complexes involves the reaction of nucleophilic cobalt(I) species with organic compounds. A wide range of $(Co^{I})^{-}$ species, including vitamin B_{12s} and the anion $[Co(dmgH)_2Py]^{-}$ are known. They are among the most powerful known nucleophiles towards saturated carbon and are capable of displacing halide, tosylate, carboxylate, sulphate and phosphate from the corresponding alkyl derivatives

$$(Co^{I})^{-} + RX \longrightarrow R(Co^{III}) + X^{-}$$

Indeed, the species $[Co(7,7'Me\ Salen)]^{-}$ is apparently so nucleophilic that it can displace bromide ion[65] from bromobenzene

as can the $(Co^{I})^{-}$ complexes of salen and acacen. The $[Co(salen)]^{-}$ anion can also displace trimethylamine from benzyltrimethyl ammonium or tetramethyl ammonium ions.[64] The reaction of $(Co^{I})^{-}$ complexes with alkyl halides has been used to synthesize many (organo cobalt(III)) complexes. Other nucleophilic displacements have been observed with acyl halides, anhydrides, alkenyl halides, alkynyl halides and with aryldiazonium salts. The rate studies indicate that the influence of axial bases on the nucleophilicity of $(Co^{I})^{-}$ species in most cases is small. Thus the reactivities of various bis (dimethylglyoximato) cobalt(I) ion vary by a factor less than 50, the rates of alkylation decreases in the approximate order as : No base > Py > Me_2S > PBu_3^n [57]. However, these are only qualitative results since the formation constants of the adducts have not been determined. The equatorial ligands do have a large effect on the $(Co^{I})^{-}$ nucleophiles and of those studied $[Co(salen)]^{-}$ is one of the most nucleophilic bases[57,64]. The nucleophilic reactivities of various species have been related to the logarithmic scale of nucleophilicities derived by Pearson[66] is defined as $n = \log k/k_o$ where n = nucleophilicity factor, k = second order rate coefficient for the reaction of that nucleophile with CH_3I in methanol, and k_o = corresponding rate coefficient for the reaction of methanol with CH_3I. The data in table (1) shows that $(Co^{I})^{-}$ complexes are some of the most powerful nucleophiles known and for these reasons they have been termed as supernucleophiles.

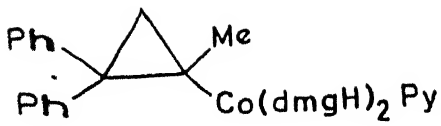
Table (1) Pearson Nucleophilicities (based on MeI) of some $(Co^{I})^{-}$ complexes and other nucleophiles[57,64]

Nucleophiles	n
MeOH	00
Cl^{-}	4.4
NH_3	5.5
I^{-}	7.4
CN^{-}	6.7
$(Co(dmgH)_2Py)^{-}$	13.8
$(Co(dmgH)_2aq)^{-}$	14.3
Vitamin B_{12s}	14.4
(Co Salen aq.)$^{-}$	14.6 and 15.6

In general, both primary and secondary alkyl halides are effective alkylating agents leading, respectively, to primary and secondary alkyl cobalt complexes. Unstrained tertiary alkyl halides do not, however, react to form tertiary alkyl cobalt complexes. Thus neither $(Co^{I})^{-}$ [67] nor hydrido (aquo) cobaloxime[68] reacts with t-butyl chloride to produce t-butyl cobaloxime. This is apparently due to the inherent instability of t-butyl cobalt complexes rather than to insufficient reactivity, Schrauzer and Deutch found isobutylene to be a product of attempted reaction of $(Co^{I})^{-}$ with tertiary butyl chloride, suggesting that a transiently formed t-butyl cobaloxime undergoes rapid β elimination (eq. 1)[69].

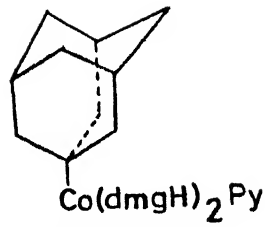
$$Me_3CCo(dmgH)_2L \longrightarrow CH_2{=}C\,Me_2 + HCo(dmgH)_2L \qquad (1)$$

However, atleast three strained tertiary organocobaloximes [4-6] has been successfully prepared via oxidative alkylation of their corresponding halides[70,71] (Fig. 2).



(60% Yield)

[4]



(11% Yield)

[5]

(3% Yield)

[6]

Fig. 2

The situation for cobalt corrins is somewhat more complex, presumably because the cobalamin chelating systems have considerably more stringent steric requirements than the dimethylglyoximato and other structurally simpler systems[72]. For instance, although Cob(I) alamin reacts rapidly with most primary alkyl halides to produce stable primary alkylcobalamins, benzylcobalamins, produced by reaction of Cob(I) alamin and para substituted benzyl bromides and chlorides, are not sufficiently stable to be isolated, presumbaly due to steric effects[73]. Para substituted benzyl cobaloximes on the other hand, are quite stable and well characterized compounds[74]. It is interesting to note that benzyl cobalt (octa ethyl porphyrin) is also unisolable due to thermal instability[75]. The steric requirements of the cobalt corrin system seem to be dependent on the state of ligation of the trans axial position i.e. steric compression at one axial ligand position increases the steric requirements for the trans axial ligand. For instance, while isopropylcobinamide is a reasonably stable material, isopropylcobalamin is not sufficiently stable to survive isolation and purification[76,77,78]. Similar arguments on the steric requirement have been put forth by Bordie[79].

Among the other reactions of $(Co^{I})^{-}$ species it can attack at a saturated carbon centre and effect ring opening[80].

$$(Co^{I})^{-} + R\ \overbrace{CH\text{-}CH_2\text{-}O} \xrightarrow[H^+]{} R\ CH(OH)\ CH_2(Co^{III})$$

Other examples of this type of reaction have been observed with ethyleneimine, THF and β lactones[75,81]. Organocobaloximes having an activated methylene group next to a hetero atom (O,S,N) have also been synthesized[82]. In an interesting variation[83] an alkenyl cobaloxime, $[(p\text{-}ClC_6H_4)_2C{=}C(Cl)](Co^{III})$, has been synthesized by the reaction of a fully saturated organic molecule, 1,1-bis(p-chlorophenyl)-2,2,2 trichloroethane (p,p'DDT) with $(Co(dmgH)_2P_y)^{-}$. A sugar derivative of (R = 1,2,3,4 diisopropylidine-6-deoxy-6-yl-α-D galactopyranose) has been prepared from $(Co^{I})^{-}$ and iodo derivative of sugar[84]. Recently, Brown et al have synthesized carboxyalkyl, 2-alkoxyethyl and 2-aryl-2-hydroxyethyl cobaloximes and carboalkyl cobalamins by such a method[85-88].

* Unlike the oxidative alkylation, oxidative arylation of $(Co(dmgH)_2Py)^{-}$ with aryl halides has achieved little success[42,65,89]. The method is also unsuccessful with vicinal dihalides where unexpected products (acetylenes) are formed but no organocobalt complex[58].

Nucleophilic vinyl substitution (S_NV) i.e. displacement at a $C_{SP}2$ centre are much less common and until recently, less understood[90-91]. The reason is attributed to the inertness of

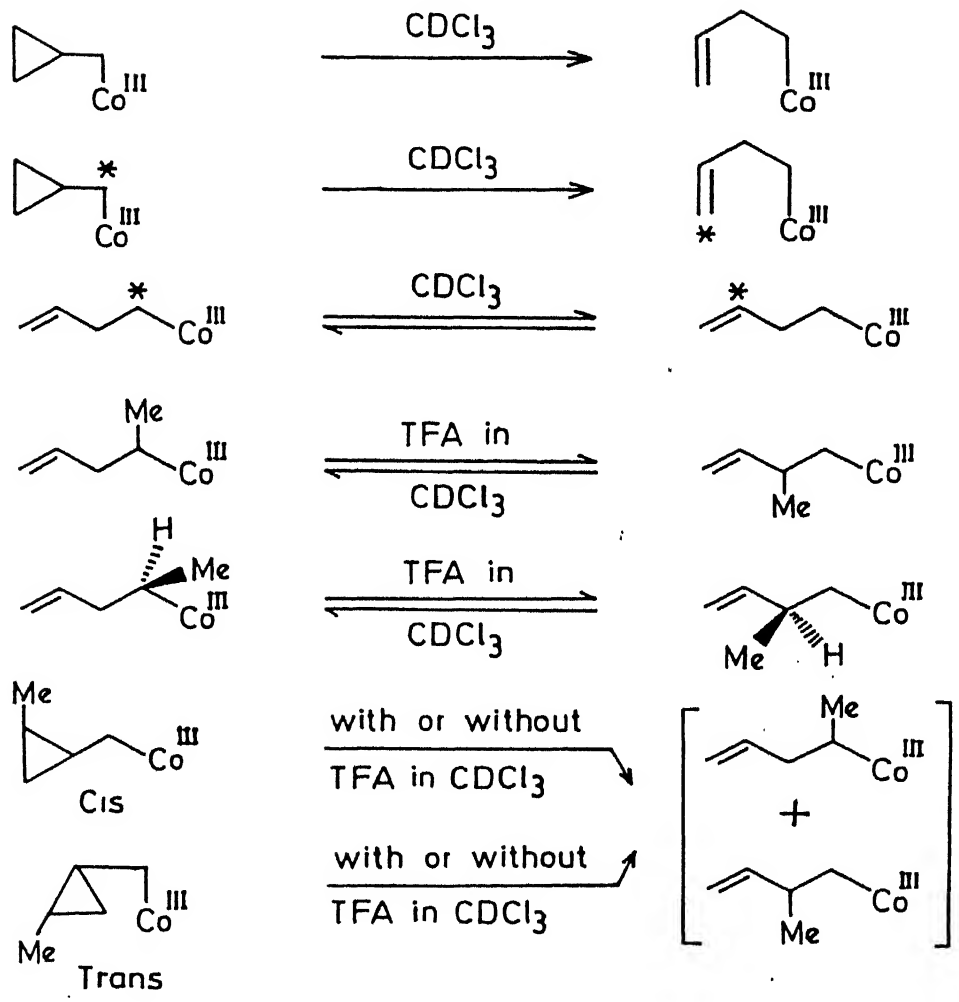
simple alkylvinyl substrates (usually halides) to S_NV process, even under forcing conditions with powerful nucleophiles[90]. Therefore, such a process usually requires activated i.e. halo, cyano, carbonyl aryl etc. substituted vinylic systems for the reaction to occur[93,94]. For example, with one exception[95], even the supernucleophile $(Co(dmgH)_2Py)^-$ anion reacts with β chloro acrylates[96] and β bromostyrene[97] and not with simple alkyl vinyl halides. Stang and Dutta[98] have very conveniently used alkyl vinyl triflates and they have synthesized a variety of stable, crystalline σ bonded vinyl cobaloximes. The reaction of isomeric (E) and (Z) vinyltriflate results in stereoconvergence. The reaction occurs more likely by a stepwise addition-elimination process with an anionic intermediate of sufficient lifetime to undergo rotation before elimination.

A.1 Generation of $(Co^I)^-$ species and its alkylation : General features

$(Co^I)^-$ species can be generated in many ways a) reduction of (Co^{II}) or (Co^{III}) reagents by $NaBH_4$ in alkaline medium b) disproportionation of (Co^{II}) to (Co^I) and (Co^{III}) in highly alkaline medium (pH ≈ 14) and c) reduction of (Co^{II}) by hydrogen in acidic, neutral or basic medium. The reduction of (Co^{II}) chelates other than cobaloximes is done with Na, K metals or their amalgams. Method a) and b) are employed most for cobaloximes however method c) is most suitable for base sensitive alkylating agents (discussed later).

In general, alkylation of a $(Co^I)^-$ complex, prepared by method a) or b) above, can be carried out in methanol. However,

σ - π Migration



Co^{III} = $Co(dmgH)_2$ Py

TFA = CF_3COOH

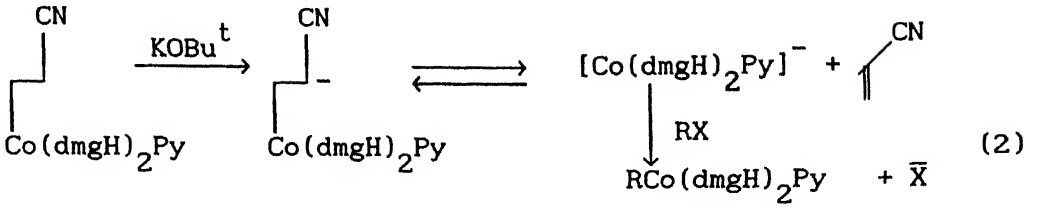
Scheme - 1.4

alkylation of the periphery of the macrocycle and reaction with the solvent methanol can prevent formation of any cobalt alkylation product. In these cases DMF can be used in place of methanol for the alkylation reaction[99].

Some cobaloximes can be prepared directly using dimethylglyoxime, and others report detail alternative routes and emphasize some difficulties encountered[100-104]. However, it is found recently that more reproducible procedures and more nearly pure products are obtained when a preformed cobaloxime is alkylated rather than obtaining the cobaloxime by a direct synthesis[99]. The majority of the cobaloximes reported in the literature have pyridine as the sixth axial ligand, but it is found that the commercially available 4-tert-butylpyridine is superior, since it decreases the solubility of the cobaloxime in water (which makes isolation of products easier) and increases the solubility of cobaloxime in organic solvent. In addition, the tert-butyl group may serve as a useful NMR marker[99].

Schrauzer's method (method b) though is the most useful method employed, it cannot be used for the synthesis of certain cobaloximes, for example, esters and thioesters of 2,2 dicarboxypropyl (pyridine) cobaloximes could not be synthesized by this method because the high pH conditions decomposed these cobaloximes[105]. Therefore, a modified method with the following strategy was used in which the generation of $(Co^{I})^{-}$ in DMSO provided a clean, non aqueous reagent of low basicity particularly useful for the synthesis of such base sensitive cobaloximes. This method, however, is no better than Schrauzer's method for the simple alkyl halides but definitely has a distinct advantage for

the base sensitive substrates.



(2)

At around the same time when the above report by Widdowson came out, a similar view was expressed by Golding et al[106] that the Schrauzer's method could not be used for the synthesis of certain cobaloximes which contained groups like esters which were prone to hydrolysis/alcoholysis[107] under alkaline conditions and for those alkylating groups containing very lipophilic alkyl groups which were insufficiently soluble in aqueous methanolic medium as used in Schrauzer's method. Furthermore, they found that cyclopropylmethyl and but-3-enyl (pyridine) cobaloximes rearranged under Schrauzer's conditions[108,109]. Their modified procedure[106] works very well for the synthesis of cobaloximes like 3,3,3-triphenylpropyl and 1-methylbut-3-enyl cobaloximes.

A.2 Mechanism of alkylation of $(Co^I)^-$

The mechanism of the reaction of $(Co^I)^-$ with alkyl halides or tosylates is not certain as was once believed to be and evidence has been presented in support of S_N2 as well as electron transfer mechanism (eq. 3-6).

S_N2 : $(Co^I)^- + RX \longrightarrow R(Co^{III}) + \bar{X}$ (3)

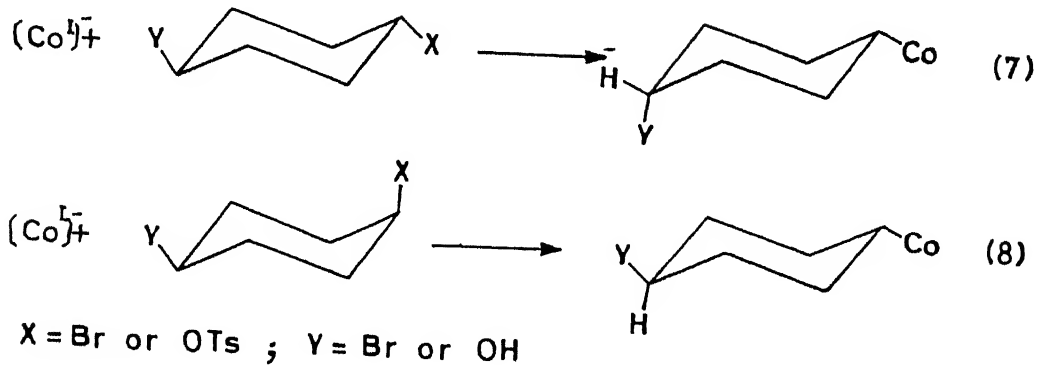
Electron transfer : $(Co^I)^- + RX \longrightarrow (Co^{II}) + R\dot{\bar{X}}$ (4)

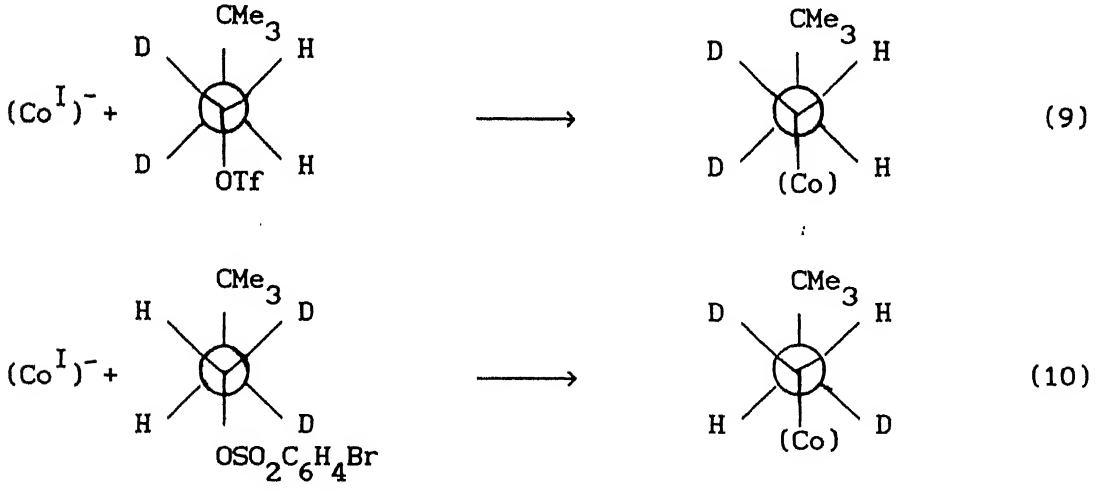
$R\dot{\bar{X}} \longrightarrow \dot{R} + \bar{X}$ (5)

$\dot{R} + (Co^{II}) \longrightarrow R(Co^{III})$ (6)

The main lines of evidence for an S_N2 process came from the kinetic studies of the reaction of $(Co^I)^-$ nucleophiles with alkyl

halides in methanolic sodium hydroxide by Schrauzer and Deutsch[67]. This conclusion was later confirmed by many studies where an inversion of configuration was observed at the displacement centre as examplified below (eq. 7-10)[110-12].





Similarly in reactions with allyl halides both S_N2 and S_N2' mechanisms may occur[113], and unlike the reactions of the same halides with conventional nucleophiles, the preference of the $(Co^I)^-$ nucleophiles for the primary carbon atom is such that only one of the two possible isomers is usually formed from both α and γ substituted allyl halides (eq. 11).

$$(Co^I)^- + \begin{matrix} Me\ CH{=}CH{-}CH_2Cl \\ or \\ CH_2{=}CH{-}CH(Cl)Me \end{matrix} \longrightarrow (Co)CH_2{-}CH{=}CH\ Me \qquad (11)$$

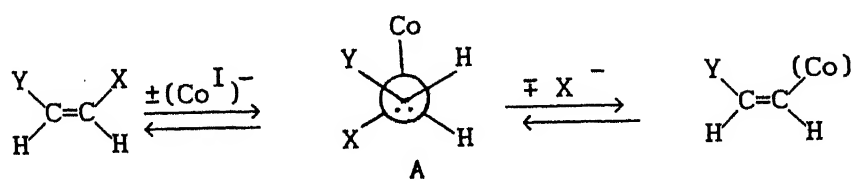
There are, however, several interesting exceptions reported. The reactions of substituted vinyl halides with $(Co^{I})^{-}$ proceeds with retention of configuration (eq. 12a-12b)[114]. Although this led to the early conclusion that the reaction proceeds via addition-elimination mechanism[114], subsequent studies on the reaction of β styryl halides with $(Co^{I})^{-}$ which confirmed this retention of configuration in both the organocobalt product and in unreacted β styryl halide and showed the order for leaving group reactivity to be I > Br > Cl > F, suggested that the reaction proceeds via concerted displacement at sp^2 carbon with retention.

$(Co^{I})^{-}$ +  (12a)

$(Co^{I})^{-}$ +  (12b)

X = Br or Cl Y = Ph or $COOCH_2CH_3$

This conclusion is confirmed by the fact that the formation of vinyl cobaloxime from vinyl chloride and cobaloxime(I) in deuterated methanol occurs without the incorporation of solvent deuterium[100]. Hence the reaction must proceed by approach of $(Co^{I})^{-}$ perpendicular to the plane of this vinyl halide (eq. 13) in which the structure A is either a transition state or intermediate with such a short life time that the rotation about the Co-C bond cannot occur, and Co-C bond formation is synchronus with C-X bond dissociation.

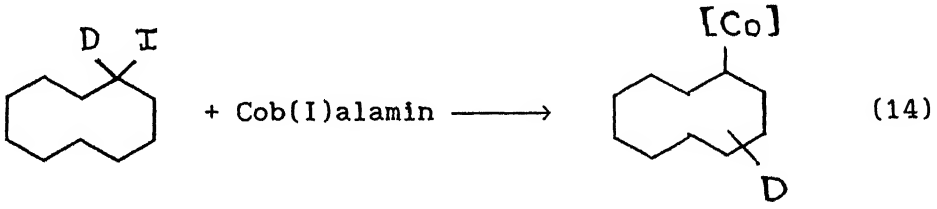
 (13)

A

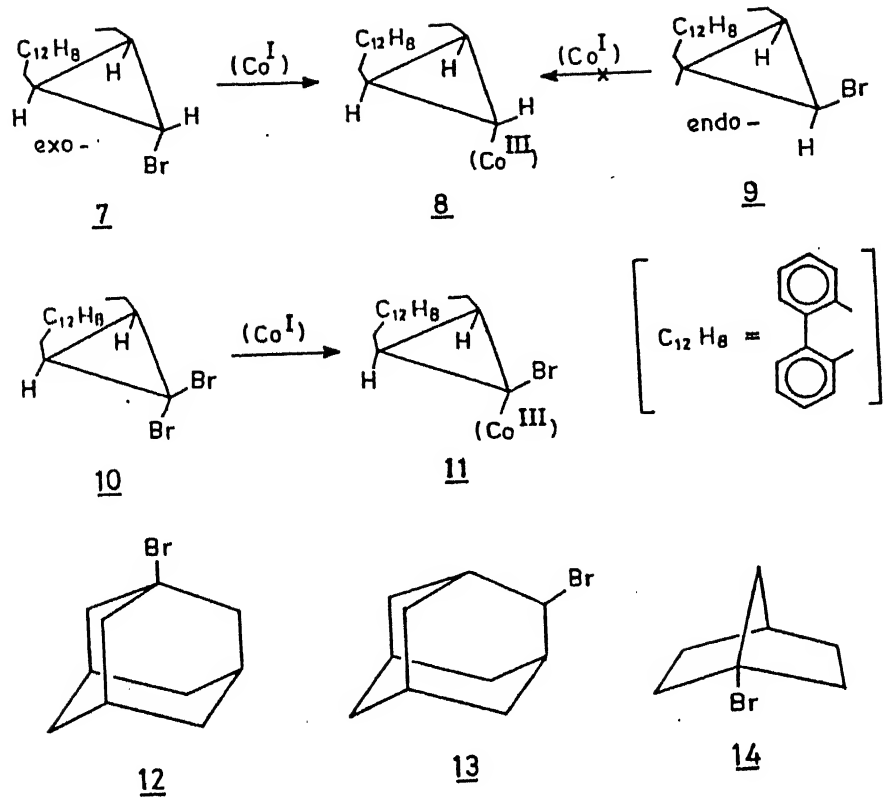
Recently an electron transfer mechanism has been proposed in a number of cases[71,115-17]. For example, the reaction of $(Co^{I})^{-}$ with different isomers of sterically hindered bromides (7,9 and 10) reveal that only the exo-structures (7 and 10) yield the corresponding cobaloximes (8 and 11) while the endo analogue (9) remains unreactive (Scheme 1.1)[115]. The mechanism either be similar to that of the displacements on vinyl halides or an electron transfer mechanism. The retention being a consequence of sheilding by the dihydrophenanthrene moiety[115].

A retentive alkylation of $(Co^{I})^{-}$ has also been reported with the sterically hindered halides (12 to 14) (Scheme 1.1) for which an electron transfer mechanism seems most likely.[71]

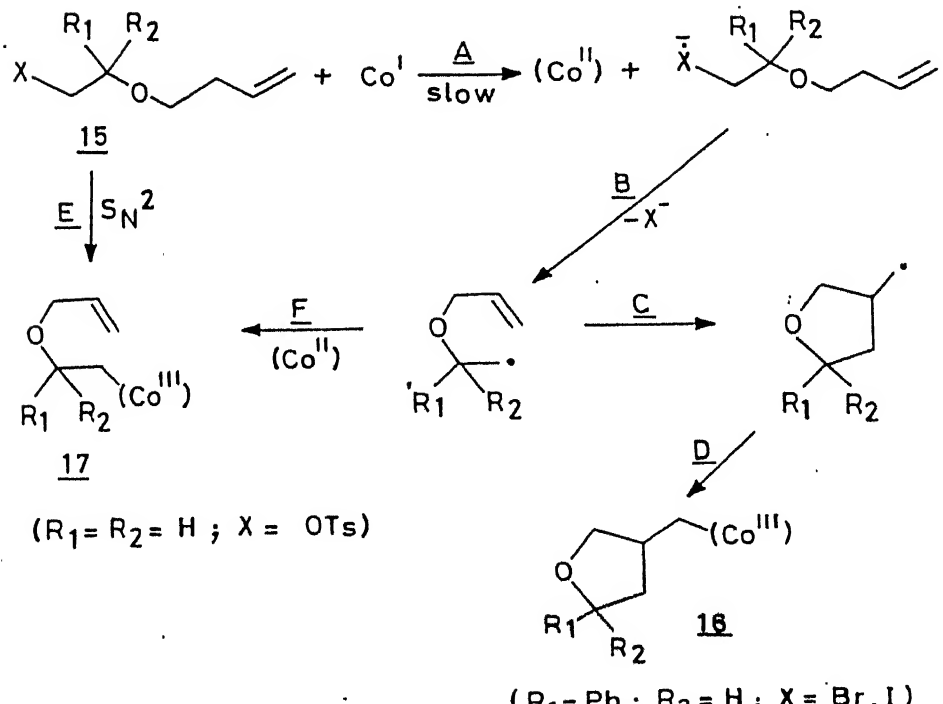
Breslow and Khanna[116] found that cyclodecyl-1-d tosylate does not react with cobalamin (1) but that the corresponding iodide reacts to produce the organocobalamin (eq. 14) in which substantial distribution of the deuterium marker over several ring carbons has occured. This was taken as an evidence for the electron transfer mechanism in which cyclodecyl radical undergoes transannular hydrogen transfer prior to its capture by cobalamin (II), a conclusion that is consistent with the failure of the cyclodecyl tosylate to react.



(14)

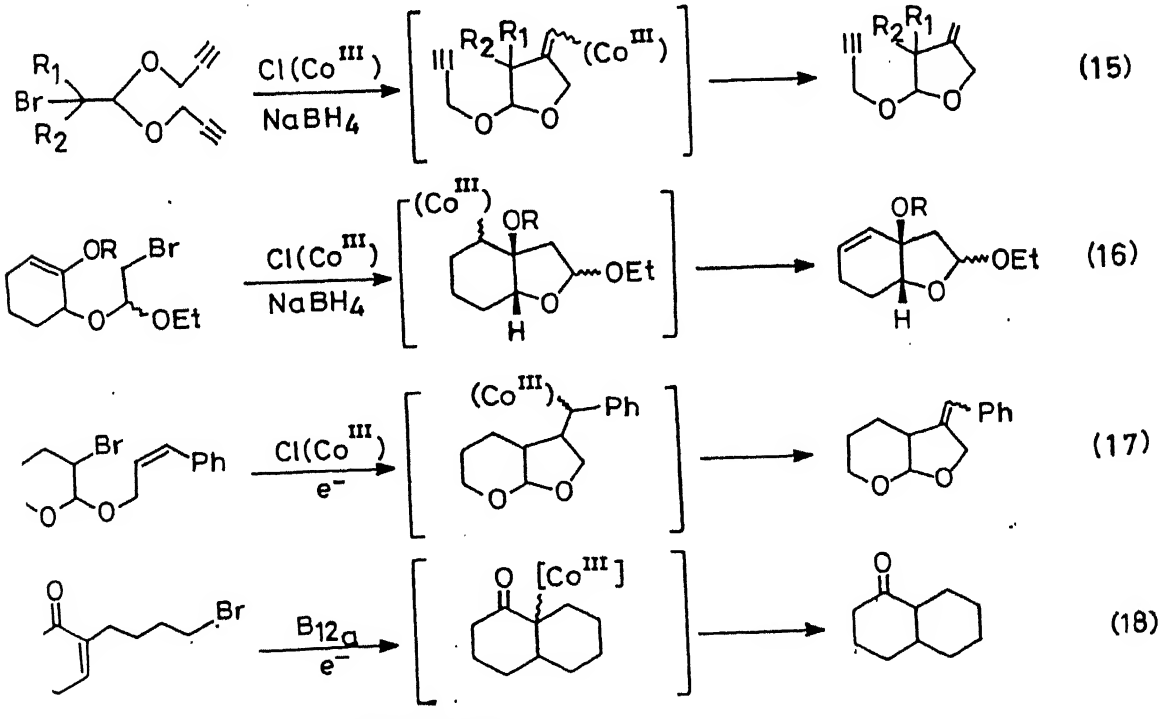


Scheme-1.1



Scheme 1.2

A conclusive evidence for the electron transfer mechanism has recently been reported by Tada et al.[117] in the reaction of (2-allyloxy) ethyl halides with $(Co^{I})^{-}$ (Scheme 1.2). (15) having a substituent at β position ($R_1 \neq H$, X = Br) gives only the cyclised product (16) via the electron transfer routes A, B, C and D. However, the corresponding reaction of (15) ($R_1=R_2=H$, X = OTs) gives exclusively the direct substitution product (17) by an S_N2 mechanism (route E). For reaction of (15) ($R_1=R_2=H$, X = Br or I) both (16) and (17) are formed which supports that both the processes occur simultaneously and even a new route (F) may also be operative.



)=Co(dmgH)$_2$Py ; [Co] = B_{12}

In many of the recently reported organic transformations (eq. 15-17) the intermediate formation of the cyclised products may involve such an electron transfer mechanism[118-20]. Scheffold has used vitamin B_{12s} in analogous studies (eq. 18)[121]. Interestingly, the alkylation of $(Co^{I})^{-}$ by 2,2 dimethyl but-3-enyl halides does not form any organocobaloximes but instead, reduction of the halide takes place for which an electron transfer mechanism has been proposed[122].

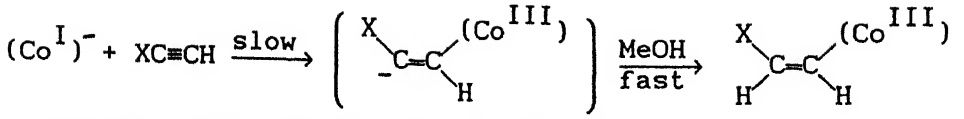
A.3 Reaction of $(Co^{I})^{-}$ nucleophiles with unsaturated molecules

The mechanism of the reaction of $(Co^{I})^{-}$ nucleophiles with olefins is not well studied. Schrauzer et al.[123] have found that in mildly basic methanolic solution, $(Co^{I})^{-}$ nucleophiles do not react directly with suitable activated olefins, such as acrylonitrile and ethylacrylate to yield σ bonded organocobaloxime but instead rapidly form species believed to be unstable $(Co^{I})^{-}$ olefin π complex (eq. 19). This then slowly rearranges to the

$$(Co^{I})^{-} + X\text{–}CH{=}CH_2 \rightleftharpoons (Co^{I})\cdots\!\parallel^{CH_2}_{CHX} \xrightleftharpoons{H^{+}} XCH_2CH_2(Co^{III}) \qquad (19)$$

(X = CN, CO_2R)

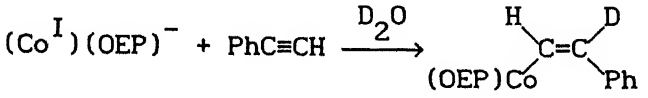
more stable σ bonded β substituted cobaloxime presumably by a trans addition of a proton from solvent, a reaction that is also reversible via base catalysed β elimination of the β substituted product. Similar reaction of $(Co^{I})^{-}$ with alkynes apparently do not involve π complex but instead occur by direct attack of the $(Co^{I})^{-}$ nucleophile on the unsaturated sp carbon with either concerted or subsequent trans addition of a proton from solvent to produce a cis-alkenyl cobalt complex (eq. 20)[97,114,124,125].



(20)

(X = Ph, COOR, CH_2OH, CF_3, CH_2COOMe)

However, for some alkynes (X = CH_2OH) a mixture of α and β substituted products are obtained. This is believed to be due to contributions of the hydridocobalt to the overall reactivity (will be discussed later). Similar stereochemistry has been observed for $(Co^I)^-$ octaethyl porphyrin[75] (eq. 21).

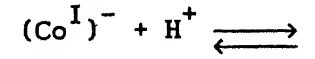


(21)

Dialkylcobaloximes of the general formula $RCo(dmgH)_2$ NC $Co(dmgH)_2Py$ have also been prepared in the literature[126,127]. Complexes containing cobalt-carbon σ bonds may also be obtained by treating certain $(Co^I)^-$ complexes with carbon dioxide, for example a deep green solution of [Co(7,7'-Pr^n(salen)K] in THF reacts with carbon dioxide at room temperature to give a deep red crystals of the adduct [Co(7,7'-Pr^n(salen)KCO_2]. The geometry about the cobalt is nearly square pyramidal and the Co-C distance is similar to those found in alkyl derivatives of [Co (salen)][128,129].

A.4 Preparation from Cobalt Hydride Complexes[35,41,55]

The $(Co^I)^-$ complexes in less basic media can pick up a proton to form covalent hydrides which can react with alkylating agents in a different manner to the $(Co^I)^-$ complexes. The existence of the equilibrium as shown below (eq. 22) was first demonstrated



(22)

with $[CoH(CN)_5]^{3-}$ which exists as such throughout the normal pH range and only gives up a proton to form $[Co(CN)_5]^{4-}$ in strongly alkaline solutions with pk of about 18-19. Similar equilibrium has been established for cobaloxime (1) but these are less basic than the pentacyano compounds and may require neutral or slightly acidic media before reactions of their hydride species become important. The dark blue hydride $[CoH(dmgH)_2PBu_3^n]$ can, for example, be extracted into hexane or benzene and has a Pk of 10.5 in 50% aqueous methanol. Solution of hydrido cobalamin are obtained if hydroxocobalamin is reduced with Zn in glacial acetic acid. Hydridocobalamin and indeed most hydridocobaloximes are unstable in water especially if nitrogen bases occupy the sixth axial co-ordinating position. However, with phosphines as sixth axial ligands, hydridocobaloximes can be isolated.

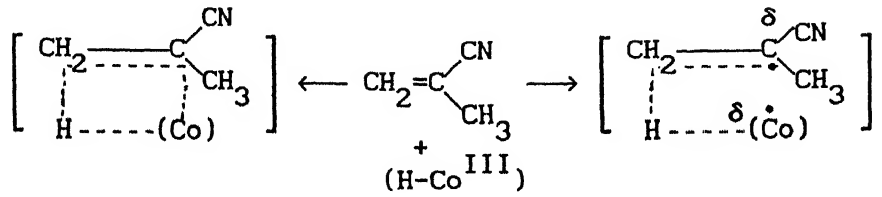
The reaction of hydridocobalt species with alkyl halides has not been studied to any significant extent, but its reaction with unsaturated reagents has been investigated in some detail. These reactions must be mechanistically quite distinct from addition of $(Co^I)^-$ nucleophiles to unsaturated compounds considering the well established difference in the mode of addition of these two cobalt reagents (eq. 23-24).

$$X\text{–}CH(CH_3)(Co^{III}) \xleftarrow{(Co\text{-}H)} X\text{–}CH{=}CH_2 \xrightarrow{(Co^I)^-} X\ CH_2CH_2(Co^{III}) \quad (23)$$

(24)

The kinetic studies by Halpern and Wang[130] on the reaction of substituted olefins with $[CoH(CN)_5]^{3-}$ ion in 50% aqueous methanol

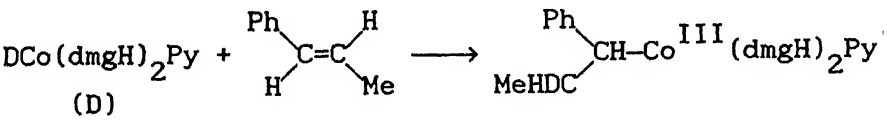
at 25°C suggests several mechanisms including one with four centre transition state (B) and the other with a biradical transition state (C) (eq. 25).



(B) (C) (25)

Halpern and Wang[130] have argued in favour of transition state (B) largely because of the question regarding the steric feasibility of the transition state (B). This is especially in view of the fact that the reactivity of CH_2=CMe(CN) exceeds that of CH_2=CHCN by an order of magnitude.

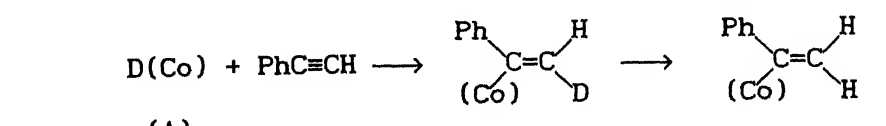
Gaudemer et al[69] have studied the following reaction (eq. 26).



(D) (26)

The reaction is shown to proceed by cis-addition of (D) to the double bond. This result may be taken either to favour the transition state (B) or to imply that the biradical character of the transition state (C) is so slight that the C-Co bond rotation cannot occur prior to formation of C-Co bond.

The stereochemistry of the addition of (D-Co^{III}) reagents to alkynes has also been studied[124] (eq. 27).



(A)

(Co) = $Co(dmgH)_2Py$ ^2_1D = (90%) ^2_1D = (10%) (27)

The addition of (A) proceeds with cis addition, however, there is no evidence to allow a discrimination between a four centre transition state (B) or one in which considerable biradical develops (C).

The following example provides another interesting variation of the addition of cobalt hydride[131] (eq. 28).

$$H\text{-}(Co^{III}) + PhNH_2 + HCHO \longrightarrow PhNHCH_2(Co^{III}) + H_2O \qquad (28)$$

The mechanism may involve the attack of the hydride on the carbinolamin formed in situ from aniline and formaldehyde.

Monothiocarbamic S-esters have apparently not been described as ligands, however, (Co^{II}) reacts under hydrogen atmosphere with monothiocarbamic vinyl ester to yield corresponding organocobaloxime[132] (eq. 29).

$$Co^{II} + R_1R_2NC(O)S\text{-}CH{=}CH_2 + \frac{1}{2}\,H_2 \xrightarrow[25°C]{MeOH} R_1R_2NC(O)S\underset{\displaystyle Co^{III}}{\underset{|}{C}}H\text{-}CH_3 \qquad (29)$$

$R_1{=}R_2{=}Pr^n$; R_1 = Et, R_2 = Bu^n; R_1 = Et, R_2 = Cyclohexyl
Co = $Co(dmgH)_2Py$

B. Preparation from Cobalt(II) complexes :

B.1 Reaction of (Co^{II}) reagent with free radicals

The reaction of an appropriately generated carbon centre radical R with a cobalt(II) chelate, a d^7 species, can provide a useful route to an organocobalt(III) complex.

$$\dot{R} + Co^{II} \longrightarrow R(Co^{III}) \qquad (30)$$

Organic hydroperoxides (and related functions) have been used as a source of organic radicals[133], for example, the reaction of

some t-alkyl hydroperoxides with (Co^{II}) macrocyclic complexes occur with a 1:2 (peroxide:cobalt) stoichiometry, the reaction being first order in both reactants[133]. The reactivity order observed is Co(dmgH)Py> $[Co(dotnH)_2]^+$> B_{12r} ≈ $[Co(tim)]^{2+}$. The basic reactions occuring are

$$RCMe_2OOH + (Co^{II}) \longrightarrow RCMe_2\dot{O} + (Co^{III})OH \quad (31)$$

$$RCMe_2\dot{O} \longrightarrow Me_2CO + \dot{R} \quad (32)$$

$$RCMe_2\dot{O} \longrightarrow RCMe\dot{O} + \dot{M}e \quad (33)$$

$$\dot{R} + (Co^{II}) \longrightarrow R(Co^{III}) \quad (34)$$

$$\dot{M}e + (Co^{II}) \longrightarrow Me(Co^{III}) \quad (35)$$

Since β fission of the alkoxy radical ($RCMe_2O$) can occur in either of two ways (eq. 32, 33), products containing both $R(Co^{III})$ and $Me(Co^{III})$ can be formed. Most of the compounds prepared by this route can be very easily prepared by the reaction of $(Co^{I})^-$ with the appropriate alkyl halide as described above (Section A). However, in cases where it is difficult to obtain the appropriate $(Co^{I})^-$ species[133,134], this radical route is preferable provided rapid and convenient synthetic quantities of $\dot{R}$ can be formed under solvent conditions in which $\dot{R}$ can react selectively to give good yields of the desired organocobalt(III) complex. The use of this radical route can also be an advantage when the reaction of alkyl halides with a cobalt(I) nucleophile such as $[Co(tim)]^+$ occur more slowly than internal reductive decomposition of the cobalt(I) species[133].

Free radicals have also been formed in situ using pulse radiolysis techniques on mixtures of alcohols and appropriate (Co^{II}) complexes. Thus the reactions of the radicals $\dot{C}H_2OH$, $Me\dot{C}HOH$, $OH\dot{C}HCH_2OH$ and $\dot{C}H_2CHO$ with $[Co\{Me_6[14]diene\}N_4]^{2+}$ give

unstable intermediates containing Co-C sigma bonds[135]. This work is of particular importance because the α-hydroxyalkyl cobalt complexes obtained, albeit transiently, have not been obtained by any other method and are of interest as model intermediates in the adenosylcobalamin requiring diol dehydrase and glycerol dehydratase enzymatic systems.

Organocobalt(III) complexes with several equatorial ligand systems (including $Co(dmgH)_2L$, Co(salen)L and several macrocyclic tetradentate ligands) have been prepared by the reaction of (Co^{II}) complexes with organic hydrazines in the presence of molecular oxygen[136] (eq. 36).

$$Co^{II}(chelate)L + R\text{-}NHNH_2 \xrightarrow[CH_3CN]{O_2} RCo^{III}(chelate)L + N_2 \qquad (36)$$

Although the mechanism of this reaction is not known, it has been speculated that oxidation of hydrazine to diazine intermediate by oxygen is catalysed by the cobalt complex. The diazine may then decompose spontaneously to N_2 and $\dot{R}$, the latter is then trapped by (Co^{II}) reagent. N_2 evolution in the reaction supports this interpretation.

Tucker[137] has used this route to obtain aryl cobalt (BAE) complexes in yields ranging from 19-70%. However, no aryl cobalt complex was obtained upon reaction with 2,4,6 tribromophenyl hydrazine.

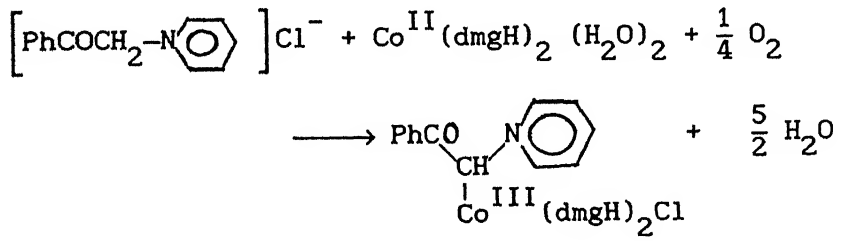
Brown and coworkers[138] have attempted to use this route to synthesize substituted arylcobaloximes with somewhat disappointing results. Thus, although p-carbomethoxyphenyl (pyridine) cobaloxime can be obtained by reaction of p-carbomethoxyphenyl hydrazine and

$Co^{II}(dmgH)_2Py$ with molecular oxygen, the yield was not appreciably better than that obtained by oxidative arylation as described earlier. However, this method has promise for the synthesis of arylcobaloximes that cannot be obtained by other routes, particularly Grignard incompatible aryl groups with electron donating groups (will be discussed later).

Pentacyanocobaltate(II) is known to react with benzene diazonium ion in water to yield phenyl cobalt complex[23,139] (eq. 37), a potentially useful reaction that has not been studied to any significant extent.

$$\left[Co(CN)_5\right]^{3-} + C_6H_5N_2^{+} \longrightarrow \left[C_6H_5\text{-}Co(CN)_5\right]^{3-} \qquad (37)$$

An interesting example showing the use of (Co^{II}) complex in the synthesis of $R(Co^{III})$ derivatives has been reported by Saito[140] (eq. 38). The mechanism of this reaction remains obscure.



(38)

Methyl radicals, generated in solution, have also been shown[35] to react with Cob(II)alamin, to yield methylcobalamin. An interesting route to alkyl and ω-carboxyalkyl cobalamins involves the oxidation of straight chain aliphatic carboxylic acids and certain dicarboxylic acids to organic radicals in the presence of Cob(II)alamin[141].

B.2 Reaction with alkyl halides :

Cobalt(II) complexes themselves are capable of inducing and terminating free radicals reactions. Such atom transfer reactions of alkyl halides with (Co^{II}) complexes in several equatorial ligand systems have been intensely studied by Halpern and coworkers[142-48] (eq. 39).

$$2Co^{II}(chelate)B + RX \longrightarrow RCo(chelate)B + XCo(chelate)B \qquad (39)$$

The following points are noteworthy

i) the rate law for reaction (39) is second order i.e., first order in each reactant.

ii) reactivity decreases markedly in the order when X = I > Br > Cl (greater than 3 order of magnitude at each step).

iii) secondary alkyl halides are more reactive than primary alkyl halides and any additional halogen or carboxyl group substitution in the α carbon significantly enhances reactivity.

The following mechanism is accepted (eq. 40, 41).

$$Co^{II}(chelate)B + RX \xrightarrow{slow} XCo(chelate)B + \dot{R} \qquad (40)$$

$$\dot{R} + Co^{II}(chelate)B \xrightarrow{fast} RCo(chelate)B \qquad (41)$$

(chelate) = $(dmgH)_2$, $(dpgH)_2$, $(MeO\text{-}dpgH)_2$, $(NO_2\text{-}dpgH)_2$, Salophen,

B = amine or phosphine ligand.

Variation of B can change the rate of halogen abstraction (eq. 40) by a factor of 10^3, the rate increases with increasing basicity of amine, although no simple pattern is observed with phosphines. Varying the equatorial glyoxime ligand has little effect. Similar reactions are observed with other halogen compounds[149] (eq. 42, 43).

$$MeI + 2[CoBr(tim)]^{+} \longrightarrow [CoBr(Me)(tim)]^{+} + [CoBr(I)tim]^{+} \quad (42)$$

$$CCl_4 + 2[Co(dmgH)_2Py] \longrightarrow CCl_3Co(dmgH)_2Py + ClCo(dmgH)_2Py \quad (43)$$

Interestingly, the reaction of p-nitrobenzyl bromide in dichloromethane with six co-ordinate complex [Co(salen) (1-methylimidazole)$_2$] proceeds by a different mechanism involving an initial electron transfer[146].

α-Bromoesters are rapidly destroyed under Schrauzer's conditions and the yield of alkoxycarbonyl cobaloximes is poor. One way to overcome this problem is to use a method described under 1.5(A1) (eq. 2, p. 15) where (Co^{I}) is used under less acidic conditions. Since it is little cumbersome and requires the synthesis of cyanoethyl cobaloxime as a starting material, Widdowson and Roussi[150] have developed an efficient and technically simple method. The method uses the reaction of $Co^{II}(dmgH)_2Py$ with the α halogenoesters in the presence of Zn wool in non aqueous medium (eq. 44, 45). The function of the Zn wool is to regenerate (Co^{II}) intermediate.

$$Co^{II}(dmgH)_2(Py)_2 \underset{Zn,\ Py}{\overset{RBr}{\rightleftharpoons}} BCo^{III}(dmgH)_2Py + \dot{R} + Py \quad (44)$$

$$\dot{R} + Co^{II}(dmgH)_2(Py)_2 \longrightarrow RCo^{III}(dmgH)_2Py + Py \quad (45)$$

The reformatsky reaction of Zn with α bromoesters is an unwanted side reaction, thus those halogens esters which react more rapidly with Zn give low yield of cobaloxime. Atom transfer reactions (eq. 39) though well studied, has not been frequently exploited as a synthetic route to organocobalt complexes. This is presumably because the yield is limited to 50% (based on cobalt) and moreover organocobalt complexes obtained this way can also be obtained,

frequently in much better yield, by the oxidative alkylation route. Unfortunately, the possible reaction of aryl halides with (Co^{II}) complexes by this route, an attractive route to the sometimes more difficult to obtain aryl cobalt complexes, has not been significantly explored.

The synthesis of organocobalt corrins via (Co^{II}) reagents and alkyl halides is somewhat hampered by the difficulties of obtaining clean one electron reduction of (Co^{III}) corrins with chemical reducing agents[133,151-54]. However, vitamin B_{12r}, cob(II)alamin, is susceptible to alkylation by alkyl halides, RX. The mechanism of the reaction when X = Cl or Br is similar to that found for other low spin cobalt(II) complexes and the reactivity increases along the sequence RCl < RBr < RI, R_2CHX < R_2MeCX and R_2CHX < R_2CClX. However, with organic iodides, the following mechanism is proposed (eq. 46, 47)[148].

$$RI + B_{12r} \underset{\longleftarrow}{\xrightarrow{fast}} B_{12r} \cdot RI \qquad (46)$$

$$B_{12r}.RI + B_{12r} \underset{\longleftarrow}{\xrightarrow{slow}} RB_{12r} + B_{12a}^{+} + I^{-} \qquad (47)$$

In general, the reactivity of vitamin B_{12r} towards organic halides is considerably lower than that of the $[Co(CN)_5]^{3-}$ anion and lies somewhere between that of (Co^{II}) complexes of dimethylglyoxime and Schiff's bases. However, it is clear that vitamin B_{12r} is a stable, well behaved species in water or methanol solution with a moderate radical type behaviour. Indeed the observed effects of highly chlorinated hydrocarbons such as DDT on coenzyme B_{12} dependent processes may be due to interaction with vitamin B_{12r} rather than vitamin B_{12s}[148]. The interaction of

ethyl diazoacetate with (Co^{II}) octaethylporphyrin also results in the formation of a Co-C bonded complex which is formed by insertion of ethoxycarbonyl carbene into a Co-N bond[155].

C. Preparation from Cobalt(III) complexes :

C.1 Reaction of (Co^{III}) reagents with Grignard reagents :

Halocobalt(III) complexes in essentially all equatorial ligand system react smoothly with organomagnesium halides and alkali metal alkyls to form organocobalt(III) complexes, frequently in good yield[30,56,156] (eq. 48).

$$XCo^{III}(chelate)L + RMgX \longrightarrow RCo^{III}(chelate)L + MgX_2 \qquad (48)$$

Though the oxidative alkylation method (Section A) is normally preferred over this method for the synthesis of alkylcobaloxime, for Grignard compatible aryl groups this method gives better yields of aryl cobaloximes (eq. 49).

$$Cl(Co^{III}) + PhC{\equiv}CMgCl \xrightarrow{THF} PhC{\equiv}C\text{-}(Co^{III}) + MgCl_2 \qquad (49)$$

Poor solubility of halocobalt(III) complexes in ether solvents and the use of many fold excess of Grignard reagents are the two major drawbacks of this method. Furthermore, it has been found that the acid work up of these reactions may lead to side products, for example, the hydrolysis of the reaction mixture with 10% HCl causes, at least in some cases, partial hydrolysis of the pyridine complex so that a mixture of aryl (pyridine) and aryl (aquo) cobaloxime may result[157] and in some cases equatorially protonated aryl-cobaloxime chloride have also been obtained[158]. The latter can be easily converted to the desired aryl (aquo) cobaloxime by treatment of the protonated organo(chloro)

cobaloxime in methanolic solution with a two fold excess of aqueous dibasic potassium phosphate.

C.2 Reaction of Co(III) reagents with stabilised carbanions, enols and carbenes :

Certain reagents capable of forming stabilised carbanion react directly with hydroxy or alkoxy cobalt(III) complexes to form organocobalt(III) complexes[159] (eq. 50).

$$ROCo(chelate)L + CH_2R'R'' \longrightarrow R'R''CH\text{-}Co^{III}(chelate)L + ROH \quad (50)$$

$R = CH_3$ or H $R' = CN$ $R'' = CN$, $CONH_2$, $COOC_2H_5$

(Chelate) = $dmgH^-$, Salen, Salph and other Schiff's bases

It was later shown that malononitrile and phenylacetonitrile react with aquocobalamin to form the corresponding organocobalamin[160].

Carbon acids including mono substituted alkynes have been shown to react with cobalt(III) reagents to form alkynyl cobalt(III) complexes[161] (eq. 51). The expected products,

$$ROCo(chelate)L + HC{\equiv}C\text{-}R' \longrightarrow R'C{\equiv}\overset{C}{\underset{1}{C}}o(chelate)L + ROH \quad (51)$$

chelate = Salen, Salph $R' = Ph$, $4\text{-}CH_3C_6H_4$, $4\text{-}BrC_6H_4$

however, is not always formed. 3-Butyn-2-ol fails to react whereas 3-butyn-2-one forms the substituted alkenyl complex $[Co\{CH{=}C(OMe)COCH_3\}Salen(Base)]$. This is apparently formed by the addition of methanol to the triple bond, presumably after the Co-C bond formation. Identical reactions also occur upon aerial oxidation of cobalt(II) complexes in solution containing acetone, acetophenone and malononitrile[162]. These reactions may be essentially the same as that involving the aquo hydroxycobalt(III)

complexes because such complexes could be formed in situ by aerial oxidation of [Co^{II}(Salen)] starting material[162].

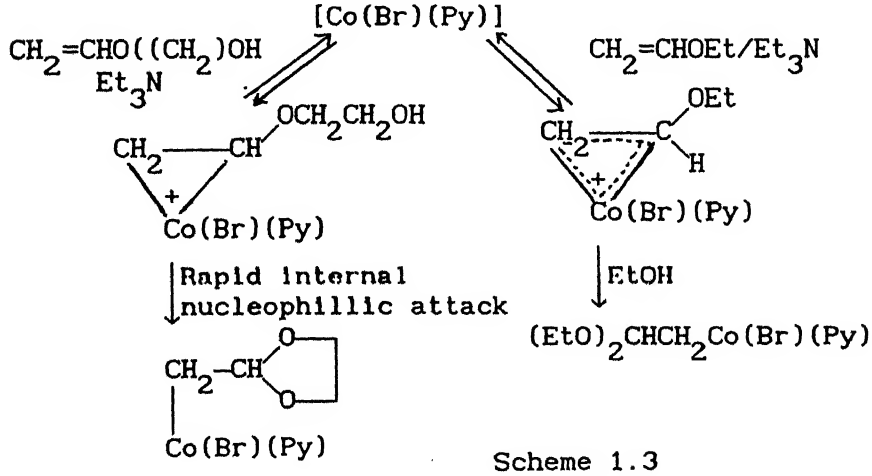
Diazoalkanes have recently been found to react with halocobalt(III) porphyrin complexes to form the substituted vinyl cobalt(III) porphyrins[163]. A mechanism has been proposed for these reactions in which an intermediate formed by insertion of a carbene derived from diazoalkane into a C-N bond of the porphyrin, followed by elimination of HX forms the vinyl cobalt product[163]. Johnson et al had previously isolated such an insertion compound from the reaction of ethyl diazoacetate with halocobalt(III) porphyrins[155,164].

Several aquo cobalt(III) complexes also react with carbon monoxide in alcoholic solution to give alkoxycarbonyl derivatives[165] (eq. 52).

$$ROH + CO + MeOCo(dmgH)_2Py \longrightarrow ROCOCo(dmgH)_2Py + MeOH \qquad (52)$$

C.3 Reactions of Cobalt(III) reagents with vinyl ethers

The reaction of cobaloximes and cobalamins with vinyl ethers in the presence of alcohols provide another route to cobalt-carbon bond[166,167] (Scheme 1.3).



Scheme 1.3

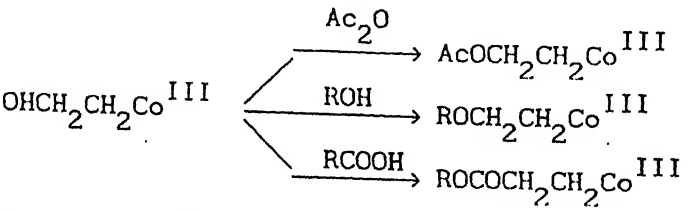
Alkynes have also been shown to add 1,4 across one of the six membered metallocyclic rings of cobalt(III) macrocyclic complex to form vinyl complexes[168].

D. Modification of axial organic Ligands

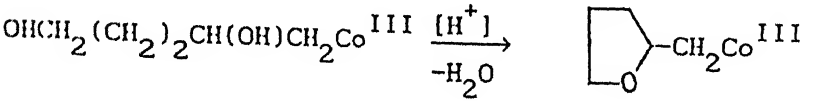
Many organocobalt(III) complexes that are difficult to synthesize by conventional routes have recently been synthesized by initially preparing a suitable chelate on which the axial or equatorial group functionalities are then modified. Although many of these modifications have been extremely simple, some are quite sophisticated and there is a great promise in such a methodology.

One of the most commonly employed modification of organic ligands is simple hydrolysis, for example, carboxymethyl and carboxyethyl cobaloximes are synthesized by hydrolysis of the corresponding methyl esters in concentrated sulphuric acid[169]. Brown and coworkers have recently prepared m and p substituted carboxyphenylcobaloximes in good yield by base catalysed hydrolysis of the respective methyl esters in 0.5 KOH in aqueous methanol[65]. Acetal hydrolysis has been very effectively used in modification of organic ligands, for example, many formyl methyl cobalamins and cobaloximes have been synthesized by acid hydrolysis of the corresponding 2,2 diethoxyethyl and 1,3 dioxa-2-cyclopentylmethyl cobalt complexes[166]. Interestingly, formylmethyl cobalamin has also been obtained by periodate oxidation of 2,3-dihydroxy-n-propyl cobalamin in aqueous methanol[155]. Golding et al have obtained a series of dihydroxyalkyl cobaloximes by hydrolysis of the cyclic acetals in

aqueous HCl[170]. Hydroxyalkyl cobaloximes have been used as precursors for many interesting transformations as illustrated below[171].

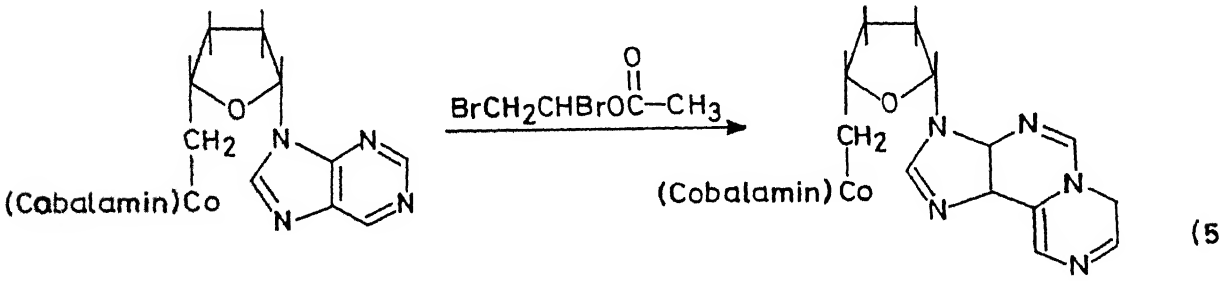


Similarly, 2,5-dihydroxy-n-pentyl cobaloxime cyclizes to tetrahydrofurfuryl cobaloxime under mildly acidic conditions[167] (eq. 53)



(53)

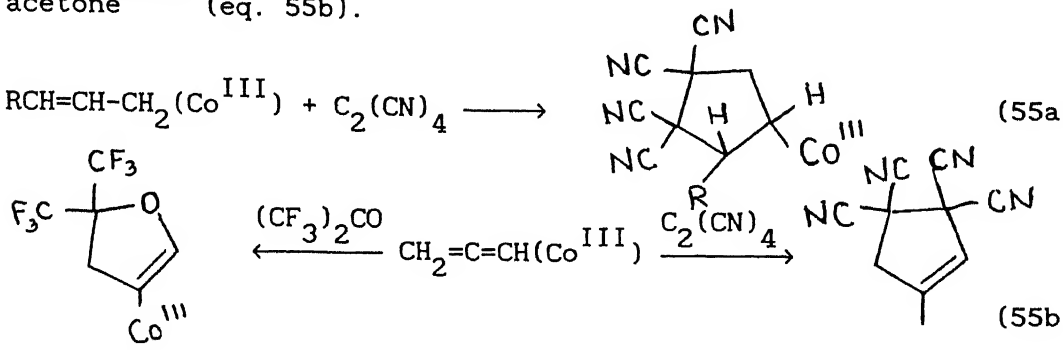
A very interesting organic ligand modification has recently been reported in which the reaction of 5'-deoxyadenosylcobalamin with α,β dibromoethylacetate at pH 4.5 produces the B_{12} coenzyme analogue 5'-deoxy(1,N^6-etheno) adenosylcobalamin[172] (eq. 54).



(5

Cycloaddition reactions have been carried out in a number of allyl, 3-substituted allyl cobaloximes with tetracyanoethylene (TCNE)[173] (eq. 55a). The reactions are believed to proceed via attack of tetracyanoethylene with concerted trans-antarafacial migration of the cobalt moiety to form the Zwitterionic π complex

intermediate with subsequent internal nucleophilic attack to yield the cyclised product. Apparently similar cycloaddition reactions occur with propadienyl cobaloxime with TCNE and hexafluoro-acetone[173b] (eq. 55b).

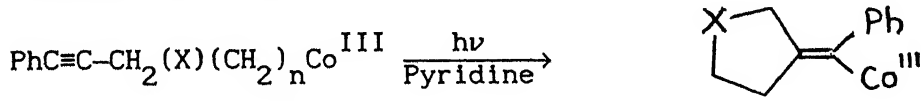


(55a)

(55b)

Many reactions have been reported in which the axial organic ligands in organocobaloximes undergo σ-π migration to give modified cobaloximes[108,109,170,174,175a] (Scheme 1.4). These reactions are of considerable synthetic utility and have played important role in the model studies of B_{12} dependent dehydrase and α-methylene glutarate mutase reaction[175b].

Recently a number of reactions have been reported in which substituted alkyl cobaloximes, on photolysis, undergo rearrangement to more stable substituted alkyl or alkenyl cobaloximes[176]. The rearrangements have been rationalised in terms of a reversible homolysis of the cobalt-carbon bond, rearrangement of the organic radical and recapture of Co^{II} fragment (eq. 56 and 57).



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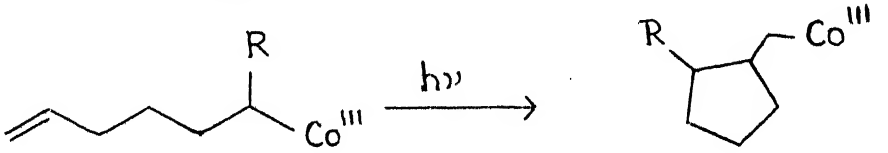
X = CH_2 n = 1,2,3

X = O n = 2,3



(57)

A similar mechanism is proposed by Ohgo and Takeuchi in the rearrangement of $XCH_2CH_2Co^{III}$ to $X\text{-}CH(Me)Co^{III}$ (X=CN, COOMe)[177].

An interesting reaction which occurs at the α carbon without disturbing the Co-C bond concerns the reactions of α-chloro and α-bromo-alkyl cobaloximes with sodium borohydride. It has been suggested that the reaction occurs by initial reduction of (Co^{III}) to (Co^{I}) followed by elimination of halide, although direct attack by hydride is also possible[55,62,178] (eq. 58 and 59).

$$[(Co)(CHXR)Py] \xrightarrow{NaBH_4} [(Co)(CH_2R)Py] \qquad (58)$$

$$(Co)(CHR)Py \xrightarrow{-HX} [Co{=}CHR(Py)] + X^- \qquad (59)$$

(hydride attack by H^- on X of (Co)(CHX R)Py)

$$[Co{=}CHR(Py)] \xrightarrow{H^+} [Co\text{-}(CH_2R)Py]$$

The stepwise replacement of halogen by hydrogen has also been demonstrated[55,62,178] (eq. 60).

$$[(Co)(CHX_2)Py] \xrightarrow{NaBH_4} [(Co)(CH_2X)(Py)] \xrightarrow{NaBH_4} [(Co)(CH_3)(Py)] \quad \ldots \quad (60)$$

Like the axial organic group (R), the axial base (B) can be very easily substituted. Such reactions are generally reversible. Both thermodynamic and kinetic aspects have extensively been studied[170].

Equatorial ligand modification can be achieved in many ways which include[158,179] i) protonation of equatorial ligand to generate $[RCo(dmgH)(dmgH_2)B]^+$ or $[R\ Co(dmgH_2)B]^{+2}$ ii) reaction with boron trifluoride to form $RCo(dmgBF_2)B$.

1.51 Novel Organocobaloximes

Among a wide variety of organocobaloximes discussed so far examples of the following kind of organocobaloximes seem few in the literature

a) Cobaloximes with tertiary α carbon atom

b) optically active cobaloximes

c) intramolecularly bridged cobaloximes

d) dicobaloximes.

a) Cobaloximes with tertiary carbon bound cobalt are difficult to synthesize and are rarely isolable.

Table 2 : The known examples of organocobaloximes with tertiary α carbon atom

R	References
$Me_2C(CN)$	169, 180
1-Methyl-2,2-diphenyl cyclopropyl	181
t-Adamantyl-	71
t-Norbornyl-	71
$MeC(Me)CH=CH_2$	182
$MeC(Et)-C\equiv CH$	182
Me(OAc)(MeCOO)C-	183
$-CCl_2COOMe$	184
$-CCl_2CN$	184
$-CCl_3$	184, 185
$^{a}Br_2PhC-$	186
$^{a}-CMe_2COOMe$	187
$RRC-C\equiv CMe$	188
R=R=Me, R,R=$-(CH_2)_5$	

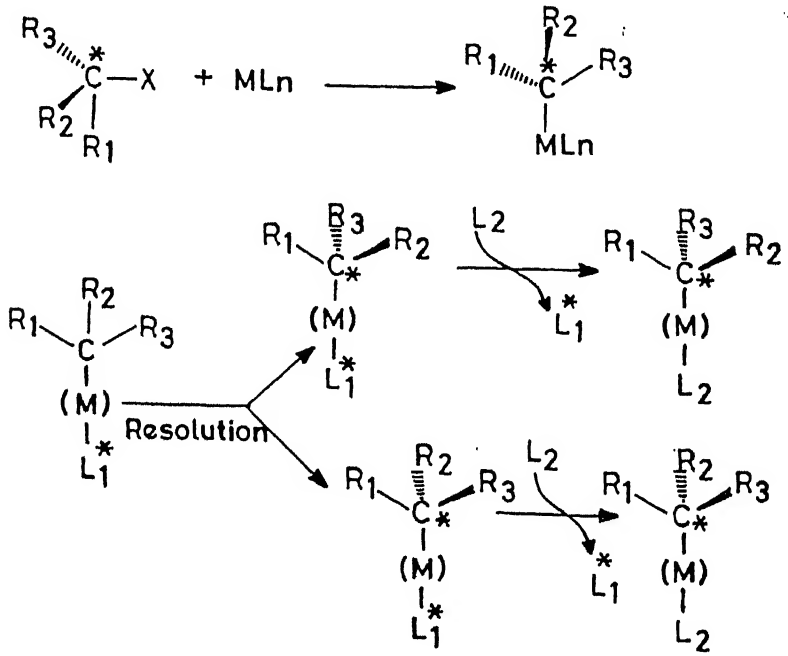
[a] suggested intermediates in the reaction of organocobaloximes

This is probably because of the weakening of the Co-C bond as there appears to be a linear relationship between the Co-C bond length and the number of substituents on the carbon attached to cobalt, for instance, the Co-C bond distances increases in the series Me < CH_2COOMe < Pr^i[145]. Furthermore, there is a tendency to eliminate Co-H under the reaction conditions. The reported examples are few and are listed in table 2.

b) Isomers are possible when the equatorial ligand in organocobaloximes or related complexes lack a plane of symmetry. All the acetamide side chains project to one side of the corrin ring and all the propionamide side chains and the nucleotide side chain to the opposite side[55]. Isomers are theoretically possible whenever the two axial ligands are different and their existence has been experimentally detected for correnoids when one axial ligand is Me, Et or CN^- and the other is water or is absent. Salen and BAE complexes although show minor deviations from planarity but they do not give rise to separable isomers[55]. All cobalt correnoids, where the ring has been formed biosynthetically are optically active.

Only one optically active organocobaloxime was known until 1973[189]. However, the synthesis of such complexes has gained momentum in the last decade. Since transition metal alkyl complexes are important intermediates in various catalytic reactions, the reactions with chiral alkyl transition metal complexes are anticipated to provide a clearer description of the elementary process of catalytic reactions, especially catalytic asymetric reactions[190-92]. In general, two basic approaches are used in the preparation of such complexes. One is based on the

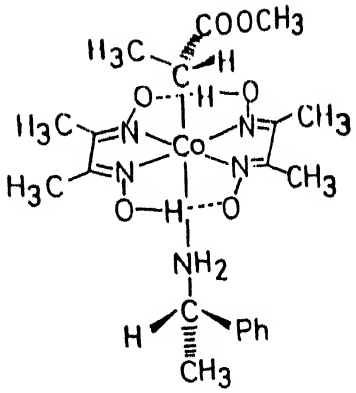
stereospecific displacement of a labile group or atom of chiral carbon compounds with metal complexes. Another method is the resolution of diastereomeric complexes with a chiral ligand (L_1^*) other than the alkyl group, followed by the displacement of the chiral ligand (L_1^*) with an achiral ligand L_2 (Scheme 1.5).



Scheme 1.5

Gaudemer et al[193] have reported the first example of chiral - atropisomeric cobaloximes in which the rotation around the atropisomeric ligand (naphthyl-vinyl bond) is inhibited by the cobaloxime substituent. These complexes are obtained by a substitution reaction of one of the enantiomers of methyl β-chloro-β-(2-methylnaphthyl) acrylate with cobaloxime (1). Representative examples are illustrated in (Fig. 3).

c) A few novel and interesting intramolecularly bridged cobaloximes have been synthesized beginning with Retey's synthesis of the bridged cobaloximes[194] (Fig 3, Structure (10), n = 10, 12), the structure of which (for n = 12) has been confirmed by X-ray



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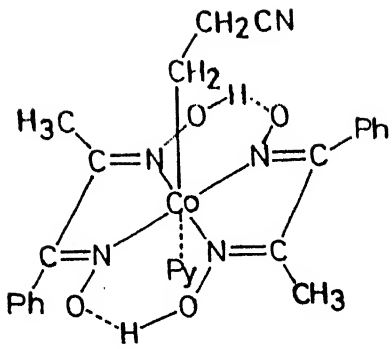

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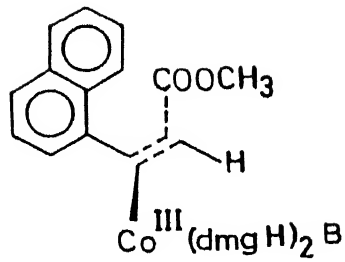

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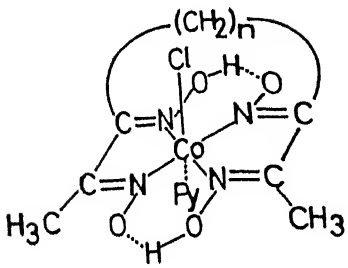

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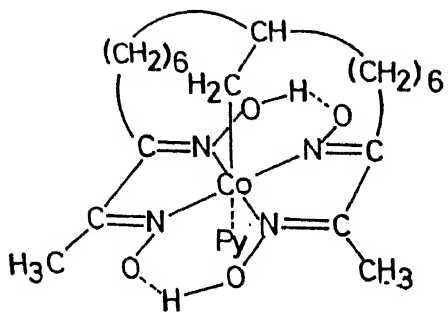

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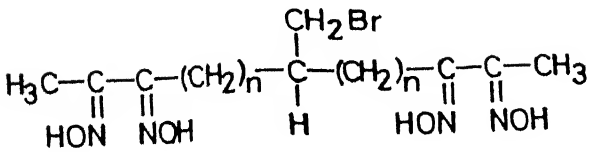

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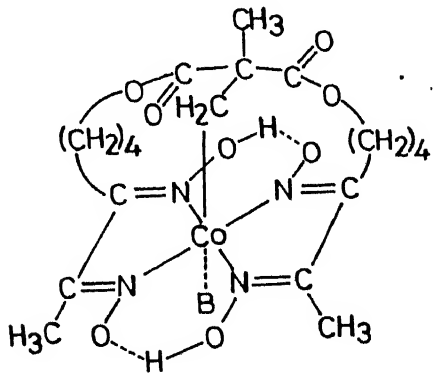


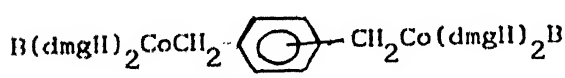
(13)

FIG. 3 NOVEL ORGANOCOBALOXIMES

crystallography[195]. Subsequently, the same workers have described the synthesis and X-ray structure of the intramolecularly bridged and alkylated cobaloximes, Structure (11), (sometimes called capped cobaloximes)[196]. Robinson[197] has described studies of the interactions of ligands such as (12), with cobalt(II) chloride under reducing conditions ($NaBH_4$) and has reported that for short chain lengths (n = 4), mostly dimeric and probably trimeric - intramolecularly alkylated cobaloximes are obtained. For n = 5 or 6, both monomeric and dimeric complexes are formed depending upon the conditions. For n = 7, only monomeric complexes are obtained including both the cis-endo and trans- configurations. Retey and coworkers[198,199] have also described the synthesis and X-ray crystal structure of (13), which has been used as a model for the active site of the adenosylcobalamin requiring enzyme methylmalonyl CoA mutase.

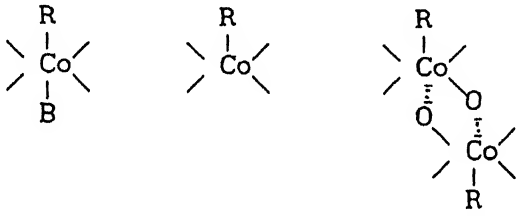
d) A number of organobridged dicobaloximes have been synthesized including those with alkyl bridges and those with aryl bridges[200]. Many bridged dicobaloximes including the neutral and anionic cyano bridged dicobaloximes have been synthesized[127,201].

$B(dmgH)_2Co(CH_2)_nCo(dmgH)_2B$



1.6 Cobaloximes : Properties and Sturcture

In general, most organocobalt(III) complexes are unstable to visible light and it is advisable to avoid light whenever the complex is in solution. However, the solid complexes are stable to visible light. The physical properties of a large number of the organocobalt(III) complexes and particularly organocobaloximes can be found in many earlier review articles[41,42,54,55]. All organocobalt(III) complexes whose magnetic susceptibilities have been determined are diamagnetic irrespective of their coordination. Organocobalt(III) complexes, in general, can exist in three different stereochemical configurations.



(a) (b) (c)

The water molecule in the aquo complex (a; B = H_2O) can be easily removed in the solid state by drying the solid over P_2O_5 or by gentle heating.

More than one hundred X-ray crystal and molecular structures have been reported with molecules containing dimethylglyoxime as the equatorial ligand[45]. The data have been thoroughly discussed earlier[45]. However, some of the points are noteworthy.

a) A large Co-C-C bond angle is observed when the coordinated ligand is tetrahedral. Indeed, the bond angle is often closer to that of sp^2 hybridised carbon atom than a tetrahedral carbon atom. It has been suggested that this rehybridisation is necessary in order to increase the overlap with the cobalt σ metal orbital and

to reduce repulsion between non-bonded electron pairs on the cobalt and the electron pairs in C-C and C-H bond[45,55]. As mentioned earlier there appears to be a linear relationship between the Co-C bond length and the number of substituents on the carbon attached to cobalt. The Co-C bond distance in adenosyl B_{12} is 2.05 A° which is consistent with the value expected for a monosubstituted methyl group[45].

b) In general, it seems that in the organocobaloximes, $RCo(dmgH)_2B$, steric interactions between the bulky bases B and the equatorial ligand system bend the equatorial ligand system towards the axial organic ligand and provoke a lengthening of the Co-C bond. Thus in $Pr^{i}Co(dmgH)_2Py$, the cobalt is displaced by 0.022 A° from the N-donor plane towards the pyridine ligand whereas in $Pr^{i}Co(dmgH)_2PPh_3$, the displacement of the cobalt towards the PPh_3 ligand is 0.017 A° [45,55].

c) Some indication of the lengthening of the Co-C bond induced by bulky ligands have also been observed in the ^{1}H-NMR chemical shift measurement in organocobaloximes[202].

d) In the complexes R $Co(dmgH)_2B$, where R is replaced by inorganic ligands like Cl^{-}, NO_2^{-} or CN^{-}, the variation in Co-B distance is found[72,45,41]. This has often been discussed in terms of the strong trans influence of the carbon bonded organic group. Indeed, both cis and trans influence has been noted in these complexes. The bending of the $(dmgH)_2$ ligand system also changes as a consequence of steric effects of the axial ligands.

1.7 Electronic Spectra

In view of the semiempirical calculations and EHMO theory, electronic structure of the cobaloximes has been considered and the results of these calculations have been useful in the analysis of the electronic spectra[203]. Three major bands appear for cobaloximes in general.

a) The absence of extensive conjugation in the cobaloxime ligand π electron system causes the energy of the $\pi-\pi^*$ transition to be at much higher energy (240 nm) than in the corrin system.

b) Between 400-250 nm there are several not well-assigned bands, the axial bases may absorb in this region, but the important low energy absorption of organocobaloximes occur between 400 and 500 nm and is believed to be typical of the presence of covalent axial bonds in view of ϵ of about 10^3. This band has been assigned to a charge transfer band (Co-C, CT). Its energy depends sensitively on the axial base and also to some extent on inductive effects and the 2s character of the axial carbon residue attached to the cobalt atom. This transition is shifted to higher energy on changing the hybridisation of the carbon residue and also on varying the axial base. Considering these arguments, the band assigned to $\sigma_2-\sigma_3$[204] has also been assigned to $d-\pi^*$ transition or d-d transition[205]. This band shifts to shorter wavelength as the alkyl group becomes more electron withdrawing as well as when the donor ability of the axial base or equatorial ligand increases. The photolysis of cobaloximes in the 400-500 nm region shows that some bands coming from the axial base and from in-plane ligands are hidden underneath. Investigations on the circular dichroism of the cobalamins have also been carried out[203].

1.8 I.R. Spectra

The vibrational spectra of cobalamins and cobaloximes reflect very broad generalities. Thus, for any alkylcobaloximes, the band at 1560 cm^{-1} is attributed to C=N stretching frequency of dimethylglyoximato ligand and is dependent on the strength of the axial base ligand. The Co-C stretch appears in the far infrared region of the spectrum. The bands which may be used for partial characterisation are ν_{OH-O} (1720-1760 cm^{-1}), ν_{N-O} (1230-1240 and 1080-1100 cm^{-1}) and ν_{C-N}(dmgH) (510-520 cm^{-1})[62,206].

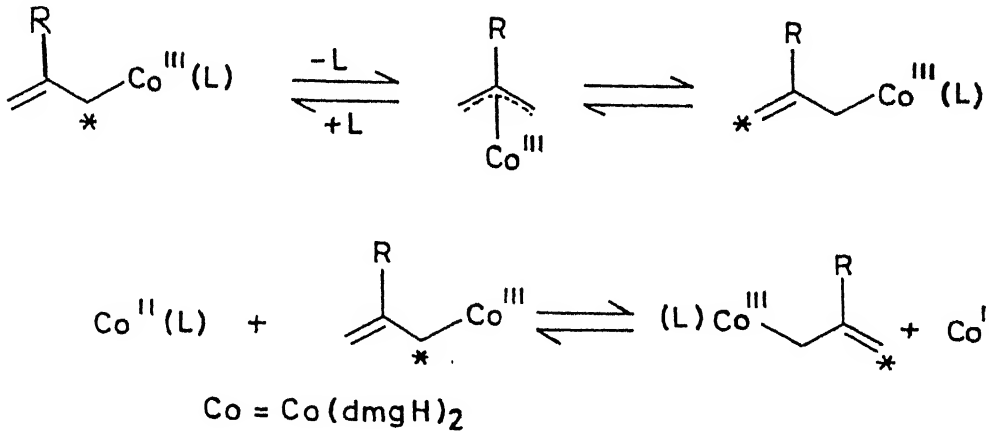
1.9 NMR Spectra

Because of the diamagnetic nature of the organocobalt(III) complexes, much information about their structure, intramolecular interactions and reactions has come from the study of ^{1}H[101,207] ^{13}C, ^{19}F and ^{59}Co NMR spectroscopy[208]. Since cobaloxime(II), a d^7 species, is often present as a trace impurity in organocobaloximes, broadening of the NMR signals occurs. A common and very useful method employed to remove cobaloxime(II) impurity is its reaction with $BrCCl_3$ which gives rise to two diamagnetic species (eq. 61)[184].

$$BrCCl_3 + 2Co^{II}(dmgH)_2Py \longrightarrow BrCo(dmgH)_2Py + CCl_3Co(dmgH)_2Py \quad (61)$$

^{1}H NMR spectra of organocobaloximes are very simple provided both the axial ligands are achiral, the four methyl groups of the equatorial dimethylglyoxime ligand appear as a sharp singlet around 2.00-2.40δ. This, therefore, has been used extensively as a diagnostic peak even in the crude samples. In complexes, $RCo(dmgH)_2B$, in which either of the two axial ligands is asymmetric, two diastereotopic pairs of methyl groups are present

and this may result in the presence of two different methyl resonances in the ^1H NMR spectrum[190-92]. The temperature dependent ^1H NMR spectra of allylcobaloximes have established the occurence of two different dynamic processes[173b] (Scheme 1.6).



Scheme 1.6

The chemical shifts of the axial organic group depend upon a number of factors including the electronic effects of the axial and equatorial groups. These have been reviewed earlier[45].

1.10 Electrochemical Reduction and Oxidation

The electrochemical reduction of cobaloximes has received little attention compared to Schiff's base B_{12} models and data available for organocobaloximes are somewhat contradictory. Costa et al have shown with nonorganocobaloximes that a) axial ligands have a marked effect on the Co^{+3}/Co^{+2} reduction potential and b) the nature of the equatorial ligand governs the Co^{+2}/Co^{+1} reduction[209]. Finke, Elliot and coworkers have observed that for alkyl and nonalkyl cobaloximes, reduction is irreversible under all conditions of added ligand, solvent, temperature etc. whereas vitamin B_{12} derivatives undergo reversible electrochemical reduction[34,210]. However, Le Hoang et al found this

electrochemical reduction of organocobaloximes to be reversible for most cases in DMSO[211]. Crumbliss and Morgan have obtained a set of data which shows that as the basicity of axial base ligand increases it becomes more difficult to reduce the cobaloximes, either electrochemically or chemically[45].

Organocobaloximes can be oxidised both chemically[212,219,220] and electrochemically[52,212-218]. EPR data suggests that the oxidised species contains (Co^{IV})[212,221,222]. The unpaired electron is shown to reside in the hybrid molecular orbital consisting primarily of 3d character with about 30% contribution from 4p orbital[221]. Co(IV) complexes are unstable at room temperature and undergo solvent assisted dissociation at low scan rates[216]. However, it is very stable at -70°C. The decomposition of RCo^{IV}, in the presence of a nucleophile, occurs via a nucleophilic attack at the ligating carbon, yielding (Co^{II}) and R-Nu with inversion of configuration[218]. The one electron electrochemical oxidation of $RCo^{III}(dmgH)_2H_2O$ with a variety of R groups are found to correlate well with the Taft σ^* parameter for R and with pKa of RH. Recently, the kinetics and thermodynamic data obtained as a function of R for reversible one electron oxidation of $RCo^{III}(dmgH)_2.H_2O$ in CH_3CN reflect the importance of steric interaction of oxidation potentials[217].

1.11 Reactions of Organocobalt Complexes

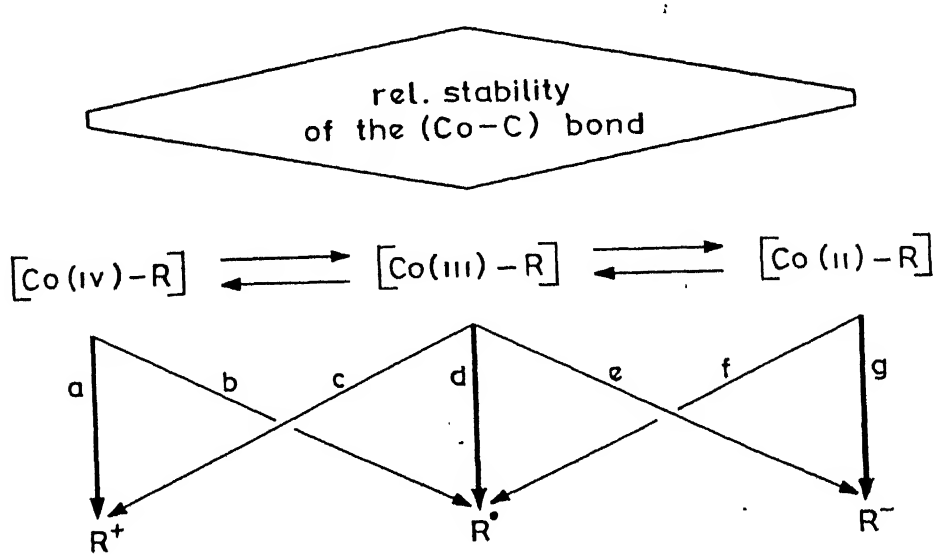
Organocobaloximes and related organocobalt complexes undergo four basic types of reactions[41,55,58,61,63,64]. a) Co-C bond cleavage b) insertion reaction c) reaction of a coordinated ligand and d) ligand replacement reactions. Since the thesis work deals mainly with the formation and cleavage of Co-C bond in

organocobaloximes, the reactions pertaining to Co-C cleavage are described in detail. The other three kind have been reviewed adequately earlier and hence do not form a part of the discussion here.

a) Co-C bond cleavage

Cobalt-Carbon bond cleavage of alkyl Co complexes (R-Co) may be induced by : reduction/oxidation of (R-Co), electrophilic, nucleophilic or free radical attack at the R group, modification within the R group, charge transfer interaction of the macrocycle with additional ligands, axial ligand exchange, light or heat, and steric interaction betwen macrocycle and alkyl group[121].

An actual cleavage is caused by combined parameters. In (Scheme 1.7) the formal routes of (Co-C) bond cleavage have been compiled[121]. Depending on the oxidation states, the R group may react as an electrophile in ($R-Co^{IV}$) path a, as radical in ($R-Co^{III}$) path d, or as nucleophile in ($R-Co^{II}$) path g. Although the reactivity of organocobalt complex is mainly controlled by its oxidation state other parameters may favour decay routes b, c, e, f[121].



Scheme 1.7

Organocobalt(III) complexes are usually stable enough to be isolated and the Co-C bond may be cleaved as a consequence of an attack by a reagent in a bimolecular reaction. On the other hand, ($R\text{-}Co^{II}$) and ($R\ Co^{IV}$) complexes are very unstable, so that 1st order decay followed by trapping of the free alkyl species by the reagent is favoured. Loss of stereochemical information at the carbon originally bound to cobalt may result from such an alternative pathway.

Redox reactions between oxidising or reducing reagents and ($R\text{-}Co^{III}$) may compete with bimolecular substitution reactions. Charge transfer complexes of the macrocycle of ($R\text{-}Co^{III}$) with electrophiles such as TCNE or transition metals e.g. $PtCl_4^{2-}$ have been shown to enhance the rate of organocobalt complex decomposition[223]. These results may be interpreted as a partial oxidation or reduction, both effecting a labilisation of the Co-C bond[224].

Most of the synthetic chemistry revolves around the cleavage of $R\text{-}Co^{III}$ complexes. Hence, an overview of these reactions is undertaken. The scheme 1.7 shows clearly that the dissociation of Co^{III}-C bond may occur by any of the three primary cleavage routes c, d and e.

(a) Cleavage by nucleophiles (route c)[41,64]

Direct nucleophilic attack at the α carbon of n-alkyl cobalt chelate is of minor importance.

A few nucleophilic displacement reactions at cobalt have been studied. Representative examples are (eq. 62a-62g).

Nucleophilic displacement at Co-C bond

$$CH_3(Co^{III}) + X^- \longrightarrow CH_3X + (Co^I)^- \qquad 62(a)$$

(X = Cl, Br, I, CN, RS, NRPh etc.)

$$CNCH_2CH_2(Co^{III}) \underset{-H^+}{\overset{-H^+}{\rightleftharpoons}} CH_2{=}CHCN \underset{(Co)}{\longrightarrow} CH_2{=}CHCN + (CO^I)^- \qquad 62(b)$$

$$CH_3CH(OH)CH_2(Co^{III}) + OH^- \longrightarrow (CH_3)_2CO + (Co^I)^- + H_2O \qquad 62(c)$$

$$OHCH_2CH(OH)CH_2\text{-}(Co^{III}) + OH^- \longrightarrow CH_3COCH_2OH + (Co^I)^- + H_2O \qquad 62(d)$$

$$R_2C{=}C{=}C(Co^{III}) + BH_4^- \longrightarrow R_2C{=}C{=}CH_2 + (Co^I)^- \qquad 62(e)$$

$$\text{cis PhCH=CH-}(Co^{III}) + MeLi \longrightarrow \text{cis PhCH=CH-Me} + Li(Co) \qquad 62(f)$$

$$\text{cis PhCH=CH-}(Co^{III}) + MeLi \longrightarrow \text{cis PhCH=CH-Li} + Me(Co^{III}) \qquad 62(g)$$

In principle, for such reactions to occur the nucleophile X^- must have a strong affinity towards saturated α carbon bound to cobalt. The possible reversibility depends upon the ability of $(Co^I)^-$ as a leaving group, the incoming nucleophile as well as their carbon basicities. The reaction should proceed to completion under aerobic conditions because oxygen will remove $(Co^I)^-$ and hence will push it to completion, whereas no apparent reaction should occur under anaerobic condition. Since reactions in both aerobic and anaerobic conditions are reported, ambiguity, therefore prevails in certain cases.

Though all the reactions described are broadly categorized under this category, there is very little evidence available, except for when X = $R\bar{S}$, for such displacement reactions. This is expected since $(Co^I)^-$ must surely be a poor leaving group, for example, in reaction (62(e)) H^- acts as a reducing agent rather than as a nucleophile[225], reactions (62(c)(d)) must be examples of base catalysed decomposition i.e. OH^- is a base in these reactions rather than a nucleophile. Several such decomposition of methyl,

ethyl, β substituted ethyl, 2 alkyoxyethyl cobaloximes have been studied and different mechanisms have been proposed for different cobaloximes[88,226]. Schrauzer's group[169,227] has studied the cleavage of 2-hydroxyethylcobalt chelates by alkali and dealkylation of alkyl cobalt(III) by mercaptide ion to form dialkylsuphides. The dealkylation of alkyl cobalt(III) complexes is readily achieved with $(Co^{I})^{-}$ or $(Rh^{I})^{-}$ supernucleophiles in what amounts to alkyl exchange between reduced metal species[228]. S_N2 mecanism has been proposed on the basis of kinetic data studies[189] (eq. 63).

$$CH_3CO^{III}(dmgH)_2B + \left[Co^{I}(chgH)_2B\right]^{-} \rightleftharpoons CH_3Co(chgH)_2B + \left[Co(dmgH)_2Py\right]^{-} \qquad (63)$$

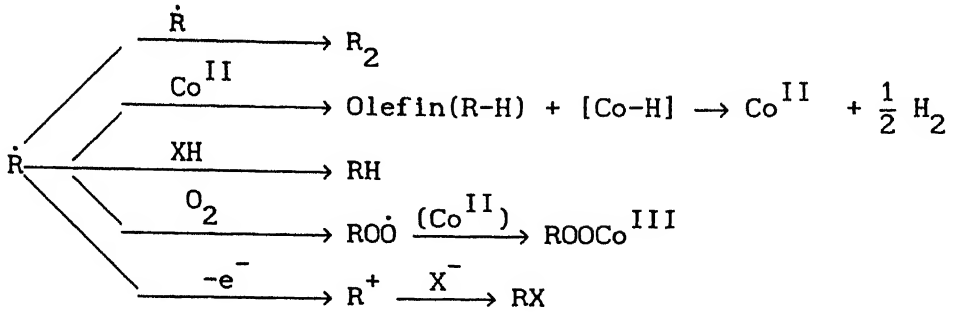
(b) Homolytic Cleavage

Homolytic Co-C bond cleavage may be induced photochemically or thermally as well as by the transfer of $\dot{R}$ to a radical acceptor.

The photolability of organocobalamins is well known and has been extensively studied[32,169,179,229-33]. Although the overall decomposition reactions often are complex, it seems likely that the principal primary photochemical process involves the homolytic cleavage of the Co-C bond to form Co^{II} and $\dot{R}$. Closely related photochemical Co-C bond cleavage process have been observed for a variety of organocobalt B_{12} model compounds including cobaloximes, Schiff base compounds and tetraazamacrocyclic cobalt compounds[229,231,234]. Flash photolytic studies have confirmed the primary Co-C homolysis[234a,235]. Such studies have shown that the

$$[Co\text{-}R] \underset{K_{-1}}{\longrightarrow} [Co^{II}] + \dot{R} \qquad (64)$$

rate of the reverse reaction of equation (64) for which the rate constant (K_{-1}) is found to be close to diffusion controlled. In addition to recombination with (Co^{II}), $\dot{R}$ radical may undergo a variety of other reactions (Scheme 1.8)



Scheme 1.8

The thermal dissociation of Co-C bond has been partly discussed earlier under stability of Co-C bond (Section 1.4). In view of the low range of bond dissociation energies (15-30 K cal $mole^{-1}$), the homolysis can occur at relatively low temperatures. The apparent thermal and photostability of organocobalt(III) compunds in anaerobic aqueous solutions often are higher than expected for such weak bonds. This has prompted many workers to suggest that the initial act is the formation of a caged radical pair which can reform the starting complex with an efficiency of ca. 0.999 but which can be decomposed by reagents such as O_2, alcohols, p-benzoquinone and spin traps[234b]. A careful study of the photochemical decomposition of alkyl aquo cobaloximes in aqueous solutions under anaerobic conditions has shown[234b] that the complexes are very photosensitive at acidities of pH 1-5 but the photoreaction is less efficient at pH 7 than at lower pH.

The following equation (eq. 65) shows that the Co-C bond cleavage reactions of sec. alkyl cobaloximes occurs with first order kinetics with ΔH values ranging from 85 kJ mol^{-1} for

$$\left[(Co)(CHMePh)Py\right] \xrightarrow[H_2]{1\ atm.} \left[(Co)Py\right] + PhCH{=}CH_2 + \frac{1}{2}\,H_2 \qquad (65)$$

The mechanism involves homolytic cleavage of the Co-C bond as the rate determining step with subsequent hydrogen abstraction rather than a concerted β hydride abstraction.

The higher alkyl cobalt(III) complexes yield aldehydes and other radical oxidation products upon aerobic photolysis. Higher alkenyl cobaloximes which posses a terminal C=C double bond give alkenyl radicals upon aerobic photolysis and undergo cyclisation reaction[64]. A number of interesting reactions also occur upon photolysis of substituted alkyl cobalt(III) complexes, the types of products formed being dependent upon the redox potential and nature of the radicals which are formed during the initial Co-C bond cleavage. Electron attracting substituents in the α position form radicals whose electron affinity may be sufficient to cause oxidation of Co(II) to Co(III). Substitutents in the β position also influences the photochemical behaviour of organocobalt(III) complexes, for example, β hydroxocobaloxime produces ethylene and acetaldehyde showing that elimination and rearrangement reactions take place. Such rearrangements have significance in the dioldehydrase reactions[55,63].

Most organocobalt(III) complexes decompose on heating without melting, a homolytic cleavage or a β hydrogen elimination reaction occurs in the process. The decomposition temperature depends upon the nature of the organic group. Also the formation of a more stable organic radical lowers the decomposition temperature. Thus α-phenylethylcobaloxime decomposes at about 90°C whereas β

phenylethylcobaloxime decomposes at about 175°C[63]. The protonation, particularly diprotonation, of the dimethylglyoximato ligand in cobaloximes enhances the rate of homolysis in solution at room temperature[41].

Several studies have been reported on homolytic Co-C bond cleavage reactions involving the transfer of radical from cobalt to radical acceptors[228,237], for example, the following displacement reaction (eq. 66) follows a first order kinetics in each reagent and occurs with inversion of configuration at the α carbon of the alkyl ligand[238]. The second order rate constant coefficients for

$$Co^{II}(dmgH)_2Py + RCo^{III}(chgH)_2Py \longrightarrow RCo^{III}(dmgH)_2Py + Co^{II}(chgH)_2Py \qquad (66)$$

this displacement reaction decreases in the sequence Me $\gg$ Et $\gg$ Pr^n $\approx$ Bu^n $\approx$ oct^n > Pr^i > Bu^i > Bu^s.

A rapid interchange between two sigma bonded allylcobaloximes occurs and the process involves a bimolecular homolytic displacement of cobaloxime(II) by attack of a similar cobaloxime(II) present as impurity at the terminal (γ carbon) of the allyl group of the organocobaloxime (eq. 67)[173].

$$Co^{*}(dmgH)_2B + \text{R-allyl-}Co^{III}(dmgH)_2Py \rightleftharpoons \text{R-allyl-}Co^{III}(dmgH)_2Py + Co(dmgH)_2Py \qquad (67)$$

Since the homolytic displacement reactions at carbon are rarely observed, this has generated a lot of interest among scientists to study these reactions. Organocobaloximes have been found to be ideal precursors for such a reaction and recently a number of such studies between σ bonded organometallic compounds with organic or

organometallic free radical precursors have been reported in the literature. The reaction, in general, is illustrated below[121,185,239(a-m),241,242]

$$RML_n + XY \longrightarrow RY + X\,ML_n \qquad (68)$$

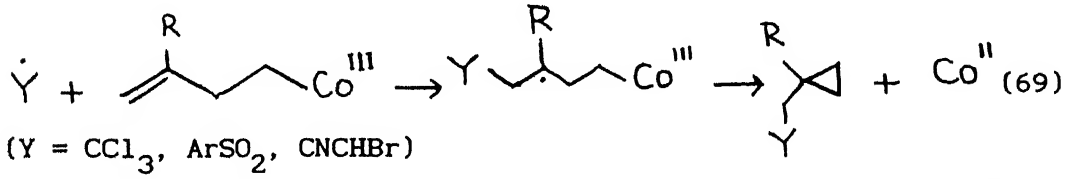
ML_n = $Ir(CO)P_2X_2$, $Rh(CO)P_2X_2$, $Co(dmgH)_2B$; X = Br,Cl; P = PPh_3, PMe_2Ph

R = alkyl, allyl, alkenyl, benzyl, etc.

Y = CCl_3, CCl_2CN, CCl_2CHO, $ArSO_2$, $ArSO_2NMe$, PhS, PhSe etc.

The key step involved in these reactions is the homolytic displacement of a low valent metal complex by attack of a C, N or S centered radical at the unsaturated or saturated carbon of the organic group in the organometallic complex[239(h,i)].

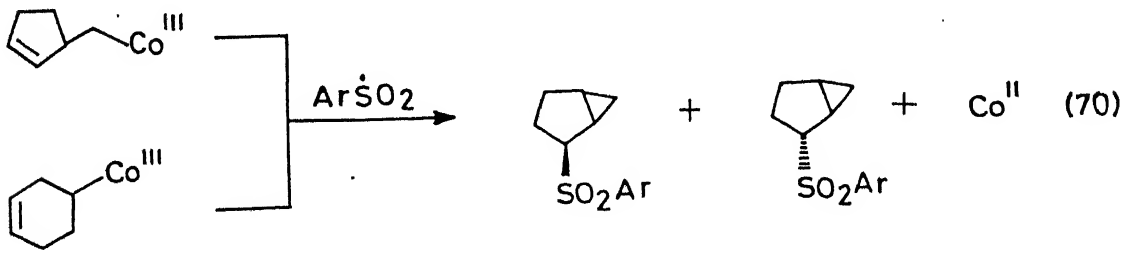
A few reactions are described in which the attack of the free radical at the unsaturated carbon centre is followed by the intramolecular homolytic displacement at the saturated α carbon (eq. 69)[185].



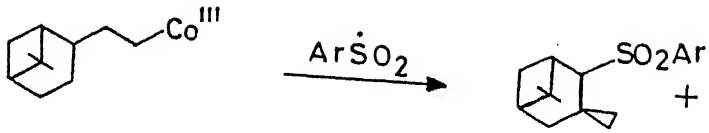
(69)

(Y = CCl_3, $ArSO_2$, CNCHBr)

Spiro and fused cyclopropane systems have been synthesized[239f,240] by the reaction of appropriate cycloalkenyl cobaloximes with free radical precursors by a similar S_H2 process (70 and 71).

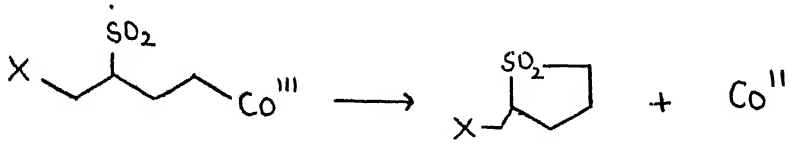


(70)



(71)

The formation of sulpholanes by the intramolecular attack of remote sulphonyl radical on the α carbon of the substituted alkyl cobaloximes (S_Hi) has been reported (eq. 72)[241a].



(72)

Free radicals, generated by Co-C bond homolysis (photochemical methods) have been trapped with many useful functional groups. Scattered examples of the study by captodative radicals with organocobaloximes are also noted in literature[241b].

(c) Electrophillic cleavage

Reactions of electrophiles with σ bonded organotransition metal complexes have been studied and reviewed in literature[128,185,239(k,m),240,241]. The reactions of organocobalt(III) and organoiron(II) complexes with electrophiles are less understood among several types of σ bonded organotransition complexes. This is because of the seemingly endless variety of reactions they undergo.

The cleanest examples of attack of electrophiles at the α-carbon of σ bonded organotransition complexes involve the d^3 organo penta aquo chromium(III) ions (eq. 73).

$$RCH_2Cr(H_2O)_6^{2+} + M^{n+} \longrightarrow RCH_2M^{(n-1)+} + Cr(H_2O)_5^{3+} \qquad (73)$$

These complexes react with widest range of electrophiles like $Hg(II)$[242], $Hg(I)$[242], $Th(III)$[243], Br_2[244], I_2[244], IBr[245], NO^+[246], NOCl and in almost all cases, the observed products are those expected for attack of the electrophile at α carbon with displacement of the highly reactive coordinatively unsaturated penta aquo chromium(III) ion. The organopentacarbonyl Mn(I), organo gold(III) and organopentacyano cobaltate(III) complexes are further examples of substrates that are not prone to oxidation, have non labile ligands and undergo a number of direct displacement reactions with electrophiles[247,248,249].

The Co-C bond of alkyl cobalt(III) complexes having an oxygen substituent on the β-carbon atom of the alkyl ligand is quite susceptible to acid and to solvent induced cleavages. The acidolysis and solvolysis of 2-hydroxy, 2-alkoxy and 2-acyloxy cobalt(III) compounds have attracted much attention since Hogenkamp and co-workers noted the lability towards acid of 2-hydroxyethyl and 2 methoxyethylcobalamin[250]. Many investigations point to the intermediacy of a π cation complex from which products are derived as first suggested by Golding[107] e.g. β hydroxy ethyl cobaloximes undergo fast and induced decomposition[251]. The formation of ethylene is believed to proceed via an intermediate π-complex between cobalt and ethylene[81,85,252] (eq. 74).

$$ROCH_2CH_2CO^{III} \xrightarrow{H^+} CH_2{=}CH_2 + ROH + (Co^{III})^+ \qquad (74)$$

(R = H, Me, Et etc)

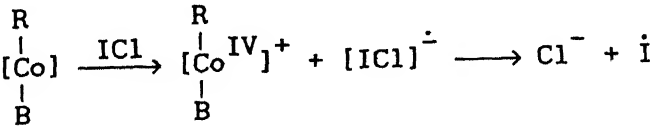
Alkyl cobaloximes are decomposed by excess trifluoroacetic acid to give a cis $Co^{II}(dmgH)_2(CF_3COO)_2$[175,253]. The degradation probably results from Co-C homolysis in the protonated alkyl

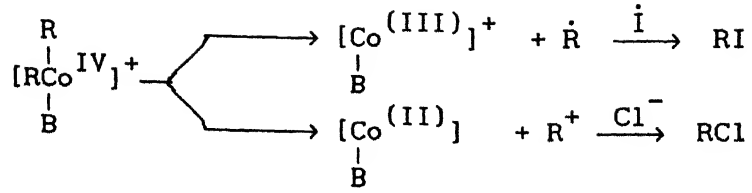
cobaloximes, followed by rearrangement to the unusual cis geometry[175,253]. The molecular structure of the 'cis cobaloxime' product has been determined by X-ray diffraction[175,253].

Styrylcobaloximes are also attacked by 1,3 benzodithiolylium tetra fluoroborate to give 2-styryl-1,3 benzodithioles[254]. Cis styrylcobaloximes showed less reactivity and regiospecificity than the trans styryl complexes. A charge transfer state was proposed which could proceed to give a cation intermediate much as in the sulfenyl chloride case, or give radical intermediates via electron transfer. The exact mechanism was not determined.

Allyl cobaloximes are attacked by the tetracyanoethylene (TCNE) to give 3,3,4,4 tetra cyanocyclopentyl cobaloximes. Such cyclo addition reaction has already been discussed in Section 1.5(D) p. 36.

Halogen studies have been carried out on a number of organocobalt(III) complexes[41,55] which mainly include their kinetic[255] and stereochemical studies[80,95,189b]. The mechanism interpreted as electrophillic substitution involves an initial one electron oxidation of the alkyl cobaloxime to give an alkyl cobalt(IV) cationic complex chloride and an iodine radical. Subsequent homolysis of the carbon-cobalt bond could be followed by coupling of the alkyl radical so formed with the iodine radical leading to racemised iodoalkane.





Recently in our laboratory, a detailed study of halogenation on a carefully designed set of substituted benzyl cobaloximes have been done[256,257].

The addition of Br_2 to alkylcobaloximes produces an EPR spectrum identical to that obtained with other chemical oxidants or electrochemically. These EPR spectra have been thoroughly studied[212,221,264] with the odd electron centered mostly on cobalt. Thus the radical cations generated by one electron oxidation of alkyl cobalt(III) complexes can best be formulated as alkyl cobalt(IV) complexes.

In contrast to the reactions of mineral acids with organocobalt chelate complexes, attack at the α-carbon by metal electrophiles occurs much more readily. Many other metal ion species react with alkyl cobalt complexes, effecting cleavage of their cobalt carbon bonds. In some of these reactions, e.g. with Tl(III), Pd(II), Me_3PbOAc, Me_3SnOAc, Me_3TeI, Me_3PI, Me_4AsI and Me_4SbI, the cleavage occurs by carbonion transfer from cobalt to the attacking metal (or non-metal) centre and the reactions are mechanistically similar to the reaction of Hg(II)[265].

Several thallium(III) and mercury(II) species including Tl^{3+} $[Tl(OH)]^{2+}$, Hg^{2+}, $[TlCl_n]^{(3-n)+}$ and $[MgCl_n]^{(2-n)+}$ $(1 \leq n \leq 4)$ have been shown to act as conventional electrophiles towards a number of cationic, anionic and neutral σ bonded organotransition metal

complexes, including the alkyl metal carbonyl ions[74,112,246,260(a-c),261]. These reactions are believed to involve the bimolecular attack of the electrophile at the α-carbon of the organometallic complex with subsequent or synchronous displacement of the transition metal ion

$$M'^{n+} + [M(CH_2)C_2H_5N^+H] \longrightarrow M^+ + [M(CH_2)R]^{n-1)+},$$

M' = Hg^{2+}, Tl^{3+}, M = $Fe(Cp)(CO)_2$[260(b)], $Mn(CO)_5$[260(c)], $Cr(H_2O)_5^{2+}$[246], $CO(CN)_5^{3-}$[261]

A comprehensive study of the kinetics of the alkylation, benzylation and arylation of mercury(II)[74,261,262] by thallium(III)[74] organocobalt compounds has been reviewed (eq. 75(a,b)).

$$R\,Co(dmgH)_2(H_2O) + Hg^{2+} + H_2O \xrightarrow{K_1} RHg^+ + Co(dmgH)_2(H_2O)_2^+ \quad (75a)$$

$$R\,Co(dmgH)_2(H_2O) + Tl^{3+} + H_2O \longrightarrow RTl^{2+} + Co(dmgH)_2(H_2O)_2^+ \quad (75b)$$

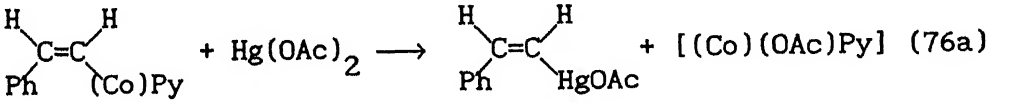
The reactions are all believed to involve a bimolecular replacement at the α carbon with retention of configuration. Two reaction paths can be envisaged (i) a direct reaction of the Hg(I) dication and (ii) reaction involving the small equal concentration of mercury(II)[263].

The stereochemistry and mechanism of the reaction have been established in the case of alkylcobaloxime as inversion via a bimolecular electrophillic reaction (S_E2). The reactions of primary alkyl cobalt(III) complexes with aq Hg^{2+} or Tl^{3+} follow second order kinetics, in some cases, acid dependent because of a rate retarding protonation of equatorial ligands. The replacement of the bridging hydrogens by BF_2 in cobaloxime complex cause sharp

reduction in reactivity with Hg(II) almost certainly resulting from electron withdrawing ability of the BF_2 groups.

While Hg(I) appear to be a good electrophile in some systems, any dealkylation of alkyl cobalt(III) complexes by Hg(I) appears to proceed via the small proportion of Hg(II) present at equilibrium[243,264].

The electrophillic displacement of cobalt from vinyl cobaloximes is faster than that from alkylcobaloxime. The reaction of cis- and trans-β styryl cobaloxime with mercury(II) acetate in acetic acid gives stereospecific formation of the corresponding cis and trans β styryl mercury(II) acetate (eq. 76a,b)[97].



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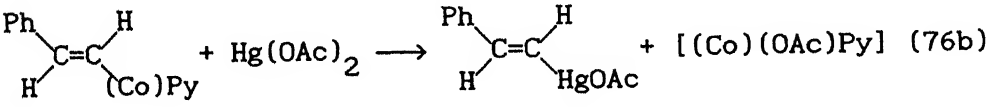


(76b)

CHAPTER - 2

REACTIONS OF ORGANOCOBALOXIMES WITH ARENE SULPHENYL CHLORIDES

2.1 AIM OF THE PROJECT

Transition metals are known to have a marked effect on the reactions of organic molecules to which they are π bonded[265]. However, much less is known about the influence of σ bonded transition metals on organic reactivity both in direction and degree.

Homolytic bimolecular displacement reactions at carbon centre are of immense importance in synthetic organic chemistry, however, examples of such kinds are few in literature[239b,240,266]. Attempts to substitute an asymmetric carbon atom have not led to any firm mechanistic conclusions though it seems probable that a S_H2 reaction at an sp^3 carbon should proceed in a manner analogous to S_N2 reaction

$$\dot{X} + RCH_2Y \longrightarrow RCH_2X + \dot{Y}$$

The scarcity of such type of reaction in literature appears more may be because of the fact that such S_H2 reactions at centres other than carbon like P, S, H, halogen and addition at unsaturated centres are more common in the systems studied so far[239b].

Mainly because of the need to start with well characterized substrates, most of the mechanistic studies of the cleavage of carbon-metal σ bond have utilized isolable, relatively stable, usually diamagnetic or organometallic complexes. Organocobaloximes fullfil all the prerequisites and have been employed as good candidates for such a reaction[240].

The essential features of these cobaloximes is the low Co-C bond energy and the inorganic radical, Co(II) species, so formed by homolysis of Co-C bond is a good stable leaving group. It neither disproportionates nor dimerises and can be maintained under anaerobic conditions in certain solvents indefinitely, unlike the majority of the conventional organic radicals[240].

Recently, the σ bonded organometallic compounds have been used as precursors for such study[240,266].

$$Cr(H_2O)_5^{2+} + RCo^{III}(dmgH)_2H_2O \longrightarrow RCr(H_2O)_5^{2+} + Co^{II}(dmgH)_2H_2O \quad \ldots\ (77)$$

$$Co^{II}(dmgH)_2Py + RCo^{III}(chgH)_2Py \longrightarrow RCo^{III}(dmgH)_2Py + Co^{II}(chgH)_2Py \quad \ldots\ (66)$$

More recently homolytic displacement by conventional organic radicals has been achieved and a number of papers have been published describing the reaction between organocobaloximes and electrophillic free radicals[128,184,185,239(i,k,m),240,241,256].

Studies of mechanism have provided valuable information about ways in which carbon metal bonds may be cleaved and the present knowledge concerns those reactions promoted by electrophillic reagents. The mechanism through which cobalt carbon bonds are cleaved and the factors that promote (or inhibit) such cleavage are of considerable importance.

Three limiting mechanisms can be formulated for bond cleavage leading to the release of Co^{III}, Co^{II} or Co^{I}. These processes are depicted in (eq. 78, 79, 80) where $[R^-]$, $[R^\cdot]$, $[R^+]$ may represent free species or bound forms.

$$(Co^{III})\text{-}R \longrightarrow (Co^{III}) + [R^-] \quad (78)$$

$$(Co^{III})\text{-}R \longrightarrow (Co^{II}) + [\dot{R}] \quad (79)$$

$$(Co^{III})\text{-}R \longrightarrow (Co^{I}) + [R^+] \quad (80)$$

Besides, oxidative and reductive Co-C bond cleavage is also known. For any particular pair of reagents; an electrophilic and organometallic substrate, one may anticipate three main types of primary reactions : displacement reaction, ionic acid/base complex formation and electron transfer, which are unlikely to be restricted to a single definable site and each of them may have a variety of possible consequences.

In the mechanism of the σ bonded substrates with electrophiles, the main emphasis is in terms of the degree of change of carbon-metal bond in the primary reaction step and the site of primary attachment of the electrophile to the substrate. Reaction possibilities are : synchronous attack of the electrophile with cleavage of carbon metal bond, reaction in which the carbon metal bond is modified, reactions in which there is little influence of or on the carbon metal bond. Electrophillic attack on the metal is thus formally a two electron oxidation process liable to induce subsequent free radical reactions and is difficult to distinguish from other oxidative processes involving electron transfer. Similarly, there are many reactions of electrophiles with organometallic complexes which do not involve substantial changes in the character of the carbon metal bond. These are (a) reactions of ligands at positions remote from and barely influenced by metals, and (b) reactions which cause sufficient change in the electronic character of the metal to

influence the rate of subsequent reactions at the carbon-metal bond.

Surprisingly a wide range of different mechanism are known and these can be ascribed to the versatile character of many organometallic substrates and of electrophillic reagents. Thus the initial stage of a reaction between an organotransition metal complex and an electrophile does not necessarily involve cleavage of the carbon metal bond, though such cleavage frequently occurs in later proocesses.

Since organocobaloximes show some susceptibility towards electrophillic displacement reactions and indeed to oxidation by some of the same electrophiles, a direct heterolytic cleavage of the Co-C bond may compete with the homolytic pathway. Because of the two operating reaction pathways in a single reaction, a mixture of products is often formed. It is, therefore, desirable to look into this problem in a systematic way so that the reasons responsible for the mixed mechanism at a saturated carbon in organocobaloximes can be rationalized.

In the present study a detailed study is done on the reaction of arene sulphenyl chloride with a range of organocobaloxime under different conditions and the focus of the present work is not on the synthesis but on the rationale of mixed mechanism at a saturated carbon in organocobaloximes.

The problem of mixed mechanism is particularly aggravated by the following facts :

(a) Organocobaloximes are prone to homolysis and frequently contain traces of cobaloxime(II) which can initiate chain process even when the heterolytic process might otherwise be dominant.

(b) Arene sulphenyl halides have a high affinity for both ionic as well as free radical reaction.

In the present study, a large number of organocobaloximes (alkyl, allyl, benzyl, heteroaromatic etc) are synthesized and following mechanistic aspects are touched and tested.

1) unambigious evidence in support of a most reasonable mechanism operating in these reactions.
2) the substituent effect of metallomethyl group, $-CH_2Co^{III}(dmgH)_2Py$ on the aromatic ring and the effect of substituents in the aromatic ring on the reactivity of Co-C bond.
3) the significance of electron transfer process in such reactions.
4) the cleavage of Co-C bond vs ring substitution in the benzyl and the heteroaromatic methyl cobaloximes.

2.2. Experimental

General

All reactions were performed in oven-dried apparatus. Reaction mixtures were stirred magnetically unless otherwise specified. Reaction product solutions were concentrated using a Perfit rotary evaporator and under reduced pressure. Distilled water was used for aqueous work-ups.

Solvents and Gases

Commercial grade solvents were distilled before use. Petroleum ether used were the 40-60°C and 60-80°C fractions. Chloroform and Dichloromethane were distilled from Phosphorous pentoxide. Methanol and Ethanol were distilled from Calcium oxide. Benzene and Carbon tetrachloride were kept over anhyd. Calcium chloride and distilled after decantation. Distilled Benzene was stored over Sodium wire. Sodium dried Diethyl ether and Tetrahydrofuran were further distilled from Lithium aluminium hydride prior to use. Pyridine was distilled from Potassium hydroxide pellets.

Extra pure Nitrogen gas (IOL AR-2) was passed successively through traps containing Fieser's solution, concentrated Sulphuric acid and Potassium hydroxide pellets prior to use. However, Oxygen gas was used directly from the cylinder.

Chromatography

Analytical thin layer, preparative thick layer and flash chromatography; all were performed using Merck Silica-gel G for thin layer chromatography. Visualization of spots or bands was effected by exposure to iodine vapour.

Physical Measurements and Instruments

Boiling points (b.p.) and melting points (m.p.) are uncorrected. Melting points were determined on a FISHER-JOHNS melting point apparatus and are uncorrected.

Infrared (IR) spectra were recorded on Perkin-Elmer model-377 and 580 infrared grating spectrophotometers and are reported in wave numbers (cm^{-1}).

Electronic spectra were recorded on Cary-17D and Shimadzu UV-190 double beam spectrophotometers.

Proton magnetic resonance (^1H NMR) spectra were recorded at 60 MHz on a Jeol PMX-60 instrument, at 80 MHz on a Brucker WP-80 instrument, at 90 MHz on a Varian EM-390 instrument and at 100 MHz on a Varian HA-100 instrument. Chemical shifts are reported in parts per million downfield from internal reference tetramethylsilane (δ). Multiplicity is indicated using following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad) etc. Coupling constants are reported wherever necessary and are expressed in Hertz (Hz).

Mass spectra were recorded at RSIC, Lucknow and RSIC Madras on VG Micromass 7o7oF mass spectrometers. Principal molecular fragments are reported.

Carbon, Hydrogen, Nitrogen and Sulphur analyses were carried out at Central Micro- Analytical Lab., IIT-Kanpur and Regional Sophisticated Instrumentation Centre (RSIC), Lucknow.

Starting Materials

Allyl chloride, 3-methyl allyl chloride, cinnamyl chloride, isoprene, propargyl alcohol, 3-methyl-1-pentyn-3-ol, benzyl chloride, iodomethane, ethyl chloride, thiophene, thiophenol, p-xylene, furfuryl alcohol, 3-methyl thiophene, 4-chloro benzyl chloride, 4- nitrotoluene, 4- toluonitrile, bromine, sulphuryl chloride, N-bromosuccinimide, lithium aluminium hydride, myrtenol, HMPT, hexachlorocyclohexane, 2,4 dinitrobenzene sulphenyl chloride, cobalt(II) chloride, dimethyl glyoxime were commercial materials (mostly Aldrich or Jansson) and in general were used as such. In some cases they were either distilled or recrystallised before use.

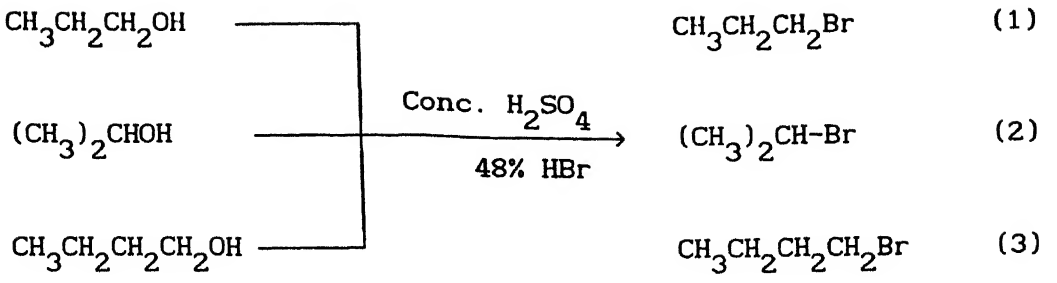
2.2.1 Synthesis of Organic Precursors

The alkyl halides, 1-Bromopropane (1), 2-Bromopropane (2) and 1-Bromobutane (3) were prepared by a standard procedure as outlined in Practical Organic chemistry by Vogel[267]. A general procedure is briefed below.

The appropriate alcohol (0.12 mol) was introduced into a round bottom flask containing 48% HBr (11.0 mL, 25g) and conc. H_2SO_4 (4.1 mL, 7.5g) and the mixture was heated to reflux. This was followed by the addition of conc. H_2SO_4 (3.25 mL, 6g). The distillate from the reaction mixture was washed successively with conc. HCl, water, 5% $NaHCO_3$ and finally with water.

1-Bromopropane (1), 80% b.p. 70-72°C, ^1H NMR (CCl_4): 1.0 (t,$-CH_3$), 1.6-2.2 (sextet, $CH_2CH_2CH_3$), 3.4 (t,$-CH_2$ Br).

2-Bromopropane (2), 81% b.p. 60°C, ^1H NMR (CCl_4): 2.1 (d,$-CH_3$), 4.5 (q, -CH).



(1)

(2)

(3)

$$CH_3(CH_2)_4CH_2OH \xrightarrow{SOCl_2} CH_3(CH_2)_4CH_2Cl \qquad (4)$$

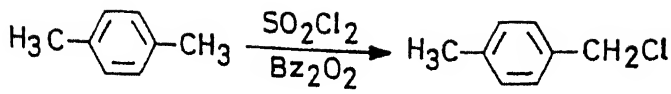
$$PhCH_2Cl \xrightarrow{NaCN} PhCH_2CN \xrightarrow[EtOH]{\text{conc. } H_2SO_4} PhCH_2COOEt \xrightarrow[Ether]{LAH}$$

$$PhCH_2CH_2OH \xrightarrow{P/Br_2} PhCH_2CH_2Br \qquad (5)$$

$$PhCH{=}CH{-}COOH \xrightarrow[Ether]{LAH} PhCH_2CH_2CH_2OH \xrightarrow{P/Br_2} PhCH_2CH_2CH_2Br \qquad (6)$$

$$PhONa + BrCH_2CH_2CH_2Br \longrightarrow PhOCH_2CH_2CH_2Br \qquad (7)$$

Scheme 2.1



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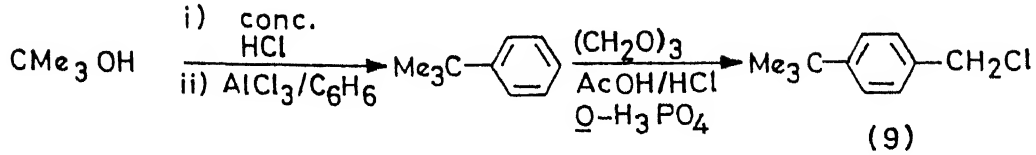

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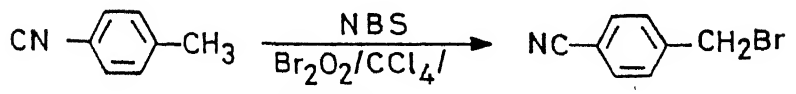

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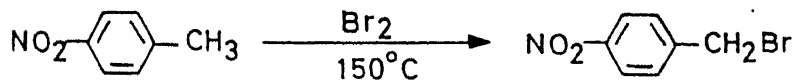

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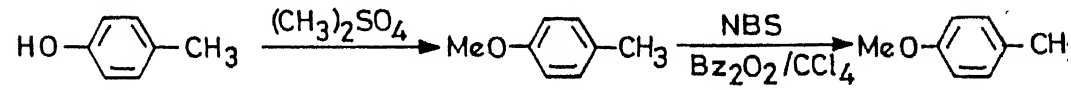

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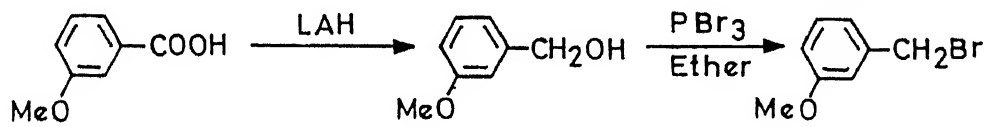

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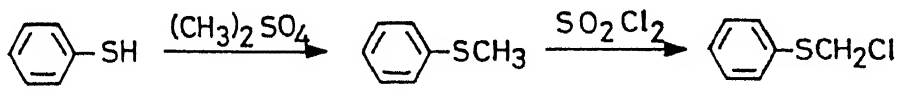

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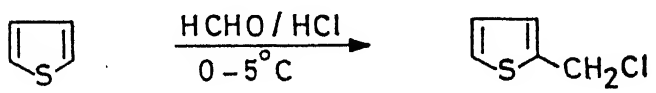

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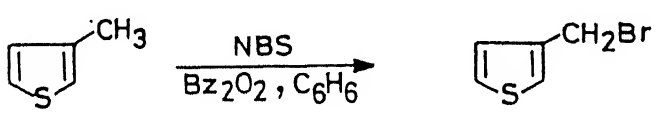

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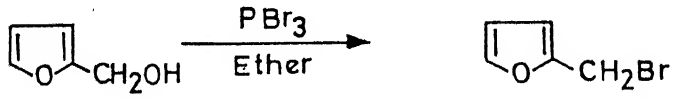

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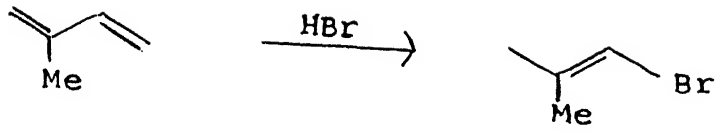
Scheme 2.1 (contd)



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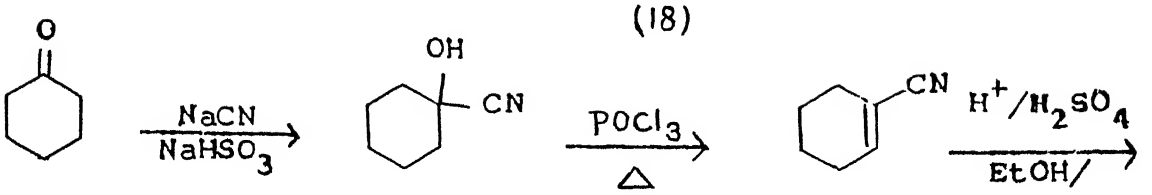

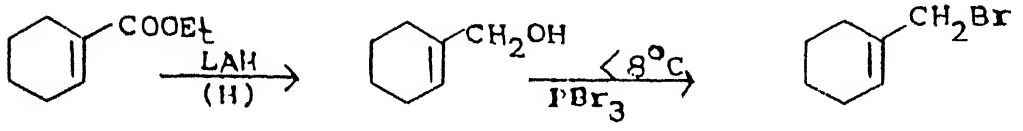

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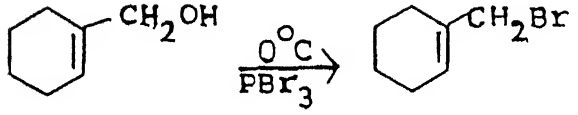

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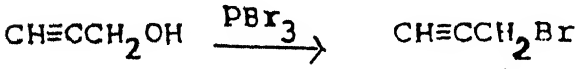

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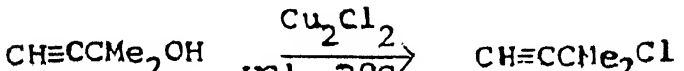

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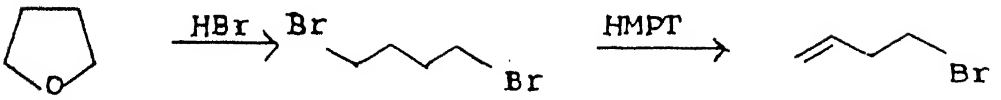

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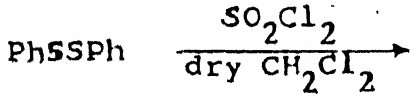
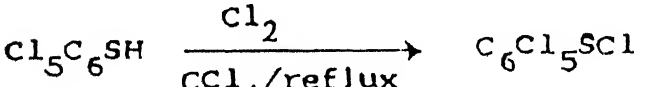
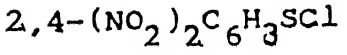


(A)



(B)



(C)

Scheme 2.1 (contd.)

1-Bromobutane (3), 80%, b.p. 104°C, ^{1}H NMR 0.9 (m,-CH_3), 1.3-2.0 (m, CH_2CH_2), 3.4 (t, -CH_2Br).

Preparation of 1-chlorohexane[267] (4)

Thionyl chloride (10.0g, 0.084 mol), was slowly added to hexanol (2.85 g, 0.028 mol). The excess thionyl chloride was distilled off and the usual aqueous work up followed by distillation gave 1-Chlorohexane (2.0g, 61%), b.p. 140-141°C, ^{1}H NMR (CCl_4) : 0.70-2.0 (bm, alkyl), 3.5 (t, -CH_2Cl).

Preparation of 1-bromo-2-phenylethane[268](5)

Benzyl cyanide (30.4g), obtained from benzyl chloride and sodium cyanide, 84%, b.p. 102°C/10 mm. ^{1}H NMR (CCl_4) : 3.7 (s, -CH_2), 7.30 (aromatic) was heated to reflux for 8 h with rectified spirit (62 mL) and conc. H_2SO_4 (27.6 mL). The usual aqueous work up followed by distillation gave ethylphenyl acetate (36.2g, 85%) b.p. 116°C/20 mm, ^{1}H NMR (CCl_4) : 1.2 (t, CH_3), 3.52 (s, CH_2Ph), 4.05 (q, CH_2CH_3), 7.1 (s, aromatic). The reduction of ethyl phenyl acetate (36.0g) with lithium aluminium hydride (8.2g) in ether gave the corresponding 2-phenyl ethanol (18.7g, 68%) b.p 116-118°C/25 mm, ^{1}H NMR (CCl_4) : 1.6 (s, -OH), 2.8 (t, -CH_2), 3.84 (t, -CH_2), 7.2 (s, aromatic). The alcohol (18.0g) on treatment with red phosphorous (1.3g) and bromine (14g, 4.4 mL) followed by the usual work up and distillation gave 1-bromo-2-phenylethane (23g, 85%), b.p. 96°C/12 mm, (Lit.[268] 98°C/12 mm)^{1}H NMR (CCl_4) : 3.0-3.3 (m, -CH_2Ph), 3.5-3.78 (m, -CH_2Br), 7.30 (s, aromatic).

Preparation of 1-bromo-3-phenyl propane[269] (6)

Cinnamic acid (7.0g, 0.044 mol) was reduced with lithium aluminium hydride (3.34g, 0.088 mol) in dry ether to give the

corresponding alcohol, 3-Phenyl propan-1-ol (5.6g, 80%), b.p. 114°C/3 mm, ^{1}H NMR (CCl_4) : 1.7-2.1 (m, CH_2Ph), 2.5-2.8 (m, CH_2-CH_2-CH_2), 3.6 (t, CH_2-OH), 7.18 (s, aromatic). The alcohol (5.4g, 0.04 mol) was brominated with bromine (1.72g, 0.022 mol) and red phosphorous (0.34g, 0.011 mol) at 250°C to give the product, 1-bromo-3-phenyl propane (6.95g, 88%) b.p. 93-95°C/8 mm. (Lit.[269] 95°C). ^{1}H NMR (CCl_4) : 2.0-2.4 (m, -CH_2Ph), 2.6-2.9 (m, CH_2-CH_2-CH_2), 3.4 (t, CH_2Br), 7.18 (s, aromatic).

Preparation of 1-bromo-2-phenoxy propane[270] (7)

A mixture of phenol (7.4g, 0.08 mol) and trimethylene bromide (20.0g, 0.09 mol) in water (40 mL) was heated to reflux and sodium hydroxide (3.0g in 500 mL of water) was added slowly. The mixture was refluxed for additional 6 h and the lower layer of the mixture was fractionally distilled to give 1-bromo-2-phenoxy propane (14.0g, 84%), b.p. 138-142°C/20 mm. (Lit.[270] 136-142°C). ^{1}H NMR (CCl_4) : 2.25 (m, -CH_2-CH_2-CH_2), 3.52 (t, CH_2O), 4.05 (t, CH_2Br), 6.78-7.4 (m, aromatic).

Preparation of 4-methyl benzyl chloride[271] (8)

A mixture of para xylene (10.0g, 0.094 mol), sulphuryl chloride (9.0g, 0.067 mol) and dibenzoyal peroxide (0.05g) in dry CCl_4 (25 mL) was heated to reflux for 2h. Excess para xylene and CCl_4 were removed and the distillation of the residue gave 4-methyl benzyl chloride (10.7g, 82%), b.p. 67°C/5 mm (Lit[271] b.p. 92°C/20 mm). ^{1}H NMR ($CDCl_3$) : 2.31 (s, CH_3), 4.48 (s, CH_2), 6.95-7.28 (m, Ph).

Preparation of 4-tert. butyl benzyl chloride[272] (9)

Tert. butyl chloride was prepared using tert-butanol and

hydrochloric acid. Friedel craft alkylation was done using benzene and tert butyl chloride to give tert butyl benzene. tert. Butyl benzene (9.6g, 0.0716 mol), paraformaldehyde (2.6g), glacial acetic acid (7.5 mL) conc. HCl (8.8 mL) and 85% ortho phosphoric acid (4.3 mL) were heated to reflux at 150°C for 20h. On cooling, the organic layer was separated, washed with water and dried over anhydrous magnesium sulphate. Distillation of the crude product gave 4-tert. butyl benzyl chloride (1.8g, 58%) b.p. 88°C/3 mm (lit[272] 114.5°C/10 mm). ^{1}H NMR ($CDCl_3$) : 1.3 (s, CH_3), 4.46 (s, CH_2), 7.2 (s, Ph).

Preparation of 4-cyano benzyl bromide[273] (10)

4-Toluonitrile (14.6g, 0.125 mol) in CCl_4 (50 mL) was added dropwise to a suspension of N-bromo succinimide (18.0g, 0.101 mol) in CCl_4 (50 mL) and dibenzoyl peroxide (0.3 g). The reaction mixture was heated to reflux for 2h. The solution was filtered hot and the filtrate was evaporated to half its volume. The crude product was recrystallised from ethanol (14.0g, 80%), m.p. 114-115°C (lit[273] m.p. 116°C). ^{1}H NMR ($CDCl_3$) : 4.52 (s, CH_2), 7.5-7.8 (m, Ph).

Preparation of 4-nitro benzyl bromide[274] (11)

4-Nitro toluene (30.0g, 0.219 mol) was brominated by bromine (36.8g, 0.48 mol) at 150°C. The reaction mixture was poured into petroleum ether (60-80°C) (400 mL). The recrystallisation of the crude product using benzene; petroleum ether mixture (1:1) gave 4-nitro benzyl bromide (22.0g, 88%); m.p. 96-97°C (lit[274] m.p. 97.5-99°C). ^{1}H NMR ($CDCl_3$) : 4.5 (s, CH_2), 7.35-8.20 (m, Ph).

Preparation of 4-methoxy benzyl bromide[275] (12)

4-Methyl anisole (12.2g, 0.10 mol), b.p. 172°C, obtained by the alkylation of p-cresol with dimethyl sulphate, was brominated with N-bromo succinimide (14.4g, 0.08 mol) in CCl_4 (60 mL). After the standard work up, the residue on distillation gave 4-methoxy benzyl bromide (13.0g, 62%), b.p. 110°C/2 mm (lit.[275] 110-113°C/2 mm). ^1H NMR ($CDCl_3$) : 3.8 (s, -OMe), 4.5 (s, $-CH_2$), 6.74-73 (m, Ph).

Preparation of 3-methoxy benzyl bromide[276] (13)

3-Anisic acid was reduced with lithium aluminium hydride to give 3-methoxy benzyl alcohol (10.0g, 0.072 mol, 90%), b.p. 129°C/9 mm). The alcohol was treated with PBr_3 (10.6g, 0.04 mol) in dry ether (200 mL). The reaction mixture was kept at room temperature for 16 h. and then hydrolysed with ice water. After the usual work up, the ethereal layer was dried over anhydrous $MgSO_4$. Evaporation of ether and the distillation of the residue gave 3-methoxy benzyl bromide (13.0g, 90%), b.p. 124°C/13 mm, (lit.[276] b.p. 123°C/13 mm). ^1H NMR ($CDCl_3$) : 3.65 (s, -OMe), 4.4 (s, $-CH_2$), 6.60-7.72 (m, Ph).

Preparation of chloro methyl phenyl sulphide[277] (14)

Thioanisole (8.4g, 0.067 mol), b.p. 188°C, ^1H NMR ($CDCl_3$) : 2.46 (s, $-CH_3$), 7.2 (s, br. Ph) obtained by the alkylation of thiophenol with dimethyl sulphate, was treated with sulphuryl chloride (9.0g, 0.067 mol) in dichloromethane (50 mL). The reaction mixture was refluxed for 3 h. After the usual work up, the residue was distilled to give chloro methyl phenyl sulphide (10.0g, 94%), b.p. 66°C/2 mm (lit.[277] b.p. 103-104°C/12 mm). ^1H NMR ($CDCl_3$) : 4.82 (s, $-CH_2$), 7.3 (s, Ph).

Preparation of 2-chloromethyl thiophene[278] (15)

A rapid stream of dry HCl gas was passed into a stirred mixture of thiophene (21.0g, 0.25 mol) and conc. HCl (10 mL) at $0^{\circ}C$. 40% Formaldehyde solution (25 mL) was added dropwise maintaining the temperature between 0-$5^{\circ}C$ after which the mixture was extracted with ether (3x25 mL). The ether layer was successively washed with water, saturated $NaHCO_3$ solution and water. It was then dried over anhydrous $CaCl_2$. Removal of solvent and distillation under reduced pressure gave 2-chloromethyl thiophene as yellow oil (10.0g, 30%), b.p. 67-68°C/10 mm (lit.[278] b.p. 73-77°C/17 mm). ^1H NMR (CCl_4) : 4.7 (s, $-CH_2$), 6.8-7.3 (m, aromatic).

Preparation of 3-bromomethyl thiophene[279] (16)

A mixture of N-bromosuccinimide (18.0g, 0.101 mol) and dibenzoyal peroxide (0.2g) was added to a refluxing solution of 3-methyl thiophene (11.0g, 0.112 mol), dibenzoyal peroxide (0.2 g) in benzene (40 mL). The mixture was immediately cooled and the succinimide was filtered out. Removal of solvent at reduced pressure and fractional distillation of the residue gave 3-bromo methyl thiophene (10.0g, 51%), b.p. 76°C/1 mm (lit.[279] b.p. 75-78°C/1 mm). ^1H NMR (CCl_4) : 4.36 (s, $-CH_2$), 7.0-7.1 (m, aromatic).

Preparation of furfuryl bromide[280] (17) in ether solution

A solution of PBr_3 (5.0g, 0.018 mol) in ether (10 mL) was added dropwise to a mixture of furfuryl alcohol (5.0g, 0.051 mol) in dry ether (40 mL) at 5-10°C. The mixture was brought to room temperature and the ether layer was decanted off. Treating first with 50% KOH solution and then with solid KOH gave a pale yellow

ether solution of furfuryl bromide which was used directly for the cobaloxime preparation. ^{1}H NMR (CCl_4) : 4.26 (s, $-CH_2$), 6.04 (s), 7.1(s).

Preparation of 3,3 dimethyl allyl bromide[281] (18)

Dry HBr gas, generated by the treatment of bromine with tetralin, was passed slowly through redistilled isoprene (8.1g, 0.122 mol) at -2 to 0°C. The crude product was fractionally distilled at 60-70°C (bath temperature) under reduced pressure. The distillate was redistilled to give 3,3 dimethyl allyl bromide as yellow oil (15.0g, 84%), b.p. 65°C/67 mm (lit.[281] b.p. 56-57°C/25 mm). ^{1}H NMR ($CDCl_3$) : 1.76 (m, CH_3), 3.86 (d, $-CH_2Br$, J = 8 Hz), 5.43 (t, =CH, J = 8 Hz).

Preparation of α-bromo-1-methyl cyclohexene[282-285] (19)

Sodium bisulphite (25g, 0.24 mol) in water (60 mL) was added with vigorous stirring during 0.5h to a cold solution of cyclohexanone (11.7g, 0.119 mol) and sodium cyanide (12.0g, 0.2 mol) in water (50 mL). After stirring for additional 4h, the reaction mixture was worked up by extraction with ether. The crude cyanohydrin obtained after solvent evaporation was taken up in pyridine and benzene (25 mL each) and was treated with a mixture of phosphorous oxychloride and pyridine (30 mL each). The reaction, worked up by the procedure of Wheelar and Lerner[283], gave 1-cyanocyclohexene (8.9g, 70%) b.p. 86°C/18 mm. ^{1}H NMR (CCl_4) : 1.45-2.54 (m, 8H, cyclohex), 6.30-6.66 (m, 1H, vinyl).

The reaction was repeated twice to produce 70.0g, 1-Cyanocyclohexene (57.6g, 0.538 mol) was heated with a mixture of conc. H_2SO_4 (60 mL), absolute alcohol and rectified spirit (70 mL

each) to afford ethyl Δ′-cyclohexene carboxylate (63.0g, 76%) b.p. 68-70°C/2mm. ^{1}H NMR (CCl_4) : 1.27 (t, 3H, CH_3, J = 15 Hz), 1.43-2.40 (m, 8H, cyclohex); 4.09 (q, 2H, CH_2-CH_3), 6.08-7.00 (m, 1H, vinyl).

The reduction of the ester (23.56g, 0.153 mol) by lithium aluminium hydride (8.73g; 0.23 mol) in solvent ether gave cyclohexene-1-methanol 13.7g, 80%, b.p. 83°C/10 mm. ^{1}H NMR (CCl_4) : 1.35-2.30 (m, 8H, cyclohex); 3.06 (s, CH_2OH), 3.79 (s, CH_2O), 5.36-5.69 (m, 1H, vinyl).

The alcohol (2.3g) was converted to α-bromo-1-methyl cyclohexene (2.8g, 78%), b.p. 94°C/10 mm (lit.[285] 80°/16 mm) by stirring with PBr_3 (0.75 mL, 2.1g) in ether at 4°C. ^{1}H NMR (CCl_4): 1.47-2.33 (bm, cyclohex), 3.86 (s, CH_2), 5.80 (bs, vinyl).

The reaction was repeated twice to produce 10.0g of the bromide.

Preparation of α-pinenyl bromide (20)

(-) Myrtenol (2.0g, 2.1 mL, 13.1 mmol) in 10 mL of absolute ether and 5 drops of pyridine was maintained at 0°C. Phosphorous tribromide (1.2g, 0.45 mL, 4.77 mmol) along with 2 drops of pyridine was added at a very slow rate with stirring to the myrtenol solution. The mixture was stirred for additional 3h and then brought to room temperature. It was washed with saturated aqueous K_2CO_3 solution and the organic layer was dried over anhyd. sodium sulphate. After removal of the solvent followed by distillation gave α-pinenyl bromide 2.25g, 79%, b.p. 70-72°C/2 mm. ^{1}H NMR (CCl_4) : 0.80; 1.28 (s, gem dimethyl), 1.09 (d, cycloalkyl), 1.25 (m, cycloalkyl), 1.83-2.62 (m, cycloalkyl), 3.82

(s, CH_2-Br), 5.60 (bs, vinyl).

Note : α-pinenyl bromide is unstable and hence must be stored in the refrigerator.

Preparation of propargyl bromide[286] (21)

PBr_3 (30.0g, 10.5 mL, 0.110 mol) containing 5 drops of pyridine was added dropwise to a mixture of propargyl alcohol (17.0g, 12 mL, 0.303 mol) and pyridine (2 mL) at 0°C. After completion of the reaction the compound was distilled at 50°C (bath temperature) and the fraction at 200 mm was collected. Redistillation afforded pure propargyl bromide (26.8g, 67%), b.p. 82-84°C (lit.[286] b.p. 82-83°C). ^{1}H NMR (CCl_4) : 2.24 (t, ≡CH), 3.88 (d, CH_2Br).

Preparation of 2,2 dimethyl propargyl chloride[287] (22)

2-Methyl-3-butyn-2-ol (16.8g, 0.190 mol) was added dropwise to a mixture of calcium chloride (11.2g), freshly prepared cuprous chloride[288] (8.0g) and copper-bronze powder (0.05g) in conc. HCl (90 mL) at 0-5°C. After 1h, the upper layer was separated from the mixture, washed successively with cold conc. HCl (2x10 mL), (water 3x25 mL), dried over anhydrous potassium carbonate and fractionally distilled under atmospheric pressure to give 2,2 dimethyl propargyl chloride (16.0g, 78%), b.p. 75°C/760 mm (lit.[287] b.p. 73-76°C/760 mm). ^{1}H NMR (CCl_4) : 1.82 (s, 6H), 2.50 (s, 1H) .

Preparation of 4-bromo-1-butene[290] (23)

(a) 1,4 Dibromobutane[289] : Redistilled THF (9.0g, 10 mL, 0.125 mol) was added with stirring to a mixture of 48% HBr(125g, 85 mL) and conc. H_2SO_4 (38g, 21 mL). The mixture was heated gently to

reflux for 3h. The lower layer of the dibromide was separated and the aqueous layer was extracted with ether (2x50 mL). The combined organic layer was successively washed with water (4x25 mL), 10% Na_2CO_3 solution (2x20 mL) and water (20mL) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent and distillation of the residue gave 1,4 dibromobutane (24g, 89%), b.p. 83°C/12 mm (lit.[289] b.p. 83-84°C/12 mm). ^1H NMR (CCl_4) : 2.6 (m, CH_2-CH_2-Br), 3.45 (t, CH_2Br, J = 5.4 Hz), 5.1 (m, $=CH_2$), 5.8 (m, =CH-)

(b) 1,4 Dibromobutane (12.04g, 0.055 mol) and freshly distilled hexamethyl phosphoric triamide (10.0g, 0.055 mol) were taken in a 50 mL claisen flask. The mixture was heated to 200-210°C (bath temperature) under dry nitrogen atmosphere. The product distilled below 100°C/760 mm was collected. It was further fractionally distilled to give 4-bromo-1-butene (7.3g, 97%) b.p. 98°C/760 mm (lit.[290] 98.5°C/760 mm). ^1H NMR (CCl_4) : 2.05 (m, $-CH_2-CH_2$), 3.45 (t, $-CH_2Br$).

Synthesis of organo sulphenylchloride

The preparative routes for the organic precursors i.e. aromatic sulphenyl halides are outlined in scheme 2.1 and the detailed procedures are given below.

Preparation of benzene sulphenylchloride[291] (A)

Freshly distilled sulphuryl chloride (20.3g, 0.15 mol) was slowly added at ambient temperature to a solution of diphenyl disulphide (32.9g, 0.15 mol) in 100 mL of CH_2Cl_2 (dry) containing 3 ml of pyridine. The solution was stirred for an additional hour and solvent was removed at ambient temperature. Subsequent distillation of the residue afforded 33.0g (76%) of dark red

benzene sulphenyl chloride b.p. 46-48°C (4 mm) (lit.[291] 49°C/4 mm). ^{1}H NMR (CCl_4) : 7.4 (s, aromatic)

The sulphenyl halides are unstable compounds as they get contaminated with acidic impurities on standing. Hence, they are stored in descicator at low temperature and are redistilled/ recrystallized just before use.

Preparation of pentachlorobenzene sulphenyl chloride[292,293] (B)

Pentachlorobenzene thiol was prepared from sodium sulphide, sulphur and hexachlorobenzene in the presence of 0.4-2.0 parts of H_2O per part hexachlorobenzene. Thus 2.5g of sulphur, 25 ml of acetone, 6.5g of 60-62% sodium sulphide, 10.2g of hexachlorobenzene and 25 ml of water were heated to reflux for 4 h and kept for 2 h to yield 90% pentachlorobenzene thiol.

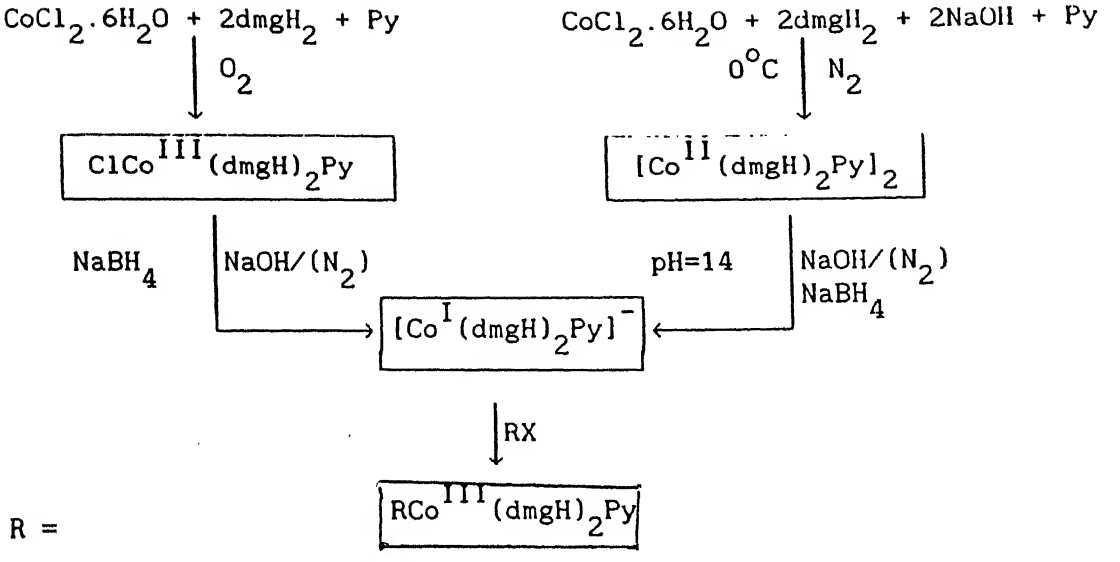
A slow stream of chlorine gas (dried by H_2SO_4) was passed through the solution of pentachlorobenzene thiol (12.5g, 0.045 mol) in 250 ml of refluxing carbon tetrachloride containing few crystals of iodine for 4 h. During this a bright red coloured developed. Evaporation of the solvent under vacuum gave 14g (92%) of pentachlorobenzene sulphenyl chloride as bright orange solid. m.p. 100°C (lit.[293] m.p. 104°C).

2.2.2 Synthesis of organocobaloximes

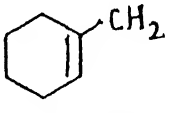
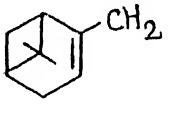
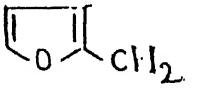
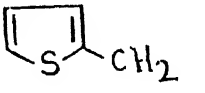
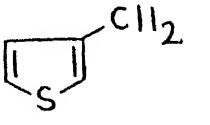
Four general methods (S1-S4) were used for the synthesis of organocobaloximes. These are described below :

Chloro(pyridine)cobaloxime(III)[294] (24)

Pyridine (3.6g, 4.0 ml) was added to a hot solution of cobalt(II) chloride hexahydrate (5.0g, 21 mmol) and dimethyl-



R =

25. CH_3
26. CH_3CH_2
27. $CH_3CH_2CH_2$
28. $(CH_3)_2CH$
29. $CH_3(CH_2)_2CH_2$
30. $CH_3(CH_2)_4CH_2$
31. $PhCH_2CH_2$
32. $PhCH_2CH_2CH_2$
33. $PhOCH_2CH_2CH_2$
34. $PhCH_2$
35. $4\text{-}MeC_6H_4CH_2$
36. $4Me_3CC_6H_4CH_2$
37. $4ClC_6H_4CH_2$
38. $4CN\text{-}C_6H_4CH_2$
39. $4NO_2C_6H_4CH_2$
40. $4MeOC_6H_4CH_2$
41. $3MeOC_6H_4CH_2$
42. $PhSCH_2$
43. $CH_2=CH\text{-}CH_2$
44. $MeCH=CHCH_2$
45. $Me_2C=CHCH_2$
46. $PhCH=CHCH_2$
47. 
48. 
49. $CH_2=C=CH$
50. $Me_2C=C=CH$
51. $CH\equiv C\text{-}CH_2$
52. $CH_2=CHCH_2CH_2$
53. 
54. 
55. 

Scheme 2.2

glyoxime (5.5g, 47 mmol) in 95% ethanol (200 ml). After cooling to room temperature, a stream of air was blown through the solution for 0.5h. The product (24) was allowed to crystallize out from solution which was filtered, washed successively with water, ethanol and ether and dried at room temperature in vacuo; yield: 5.0g (58% based on cobalt chloride hexahydrate).

Method S.1

Preparation of allyl (43-48) and but-3-enyl (52) cobaloximes

All seven cobaloximes were prepared by the following general method[294] :

Cobalt(II) chloride hexahydrate (9.52g, 40 mmol) and dimethylglyoxime (9.38g, 80 mmol) were stirred in methanol (200 ml) in a 500 ml three-necked RB flask fitted with a gas inlet tube, a pressure-equalising dropping funnel and an adapter outlet connected to a mercury trap. A stream of pure, dry nitrogen was passed through the mixture for 30 minutes. An aqueous solution of sodium hydroxide (ca. 5-6 ml, 80 mmol) was added to the mixture, followed by pyridine (3.2 ml, 40 mmol). The mixture was cooled in an ice-salt bath and aqueous sodium hydroxide (ca. 6-8 ml, 100 mmol) was added. A deep-blue solution was formed. Appropriate organic halide (40 mmol) in methanol (10 ml) was added dropwise to the mixture. The colour changed from blue to red. The solution was stirred for another 3h and brought to ambient temperature. Approximately one-third volume of solvent was evaporated under reduced pressure and the mixture was poured into water (200 ml) containing few drops of pyridine. The precipitated solid was washed with cold water (ca. 300 ml) until the washings were pale yellow. It was then washed with ether (ca. 3x25 ml) and dried in

vacuo. An analytical sample was obtained by recrystalizing the product from hot 50% aq. ethanol which was yellow to orange in colour.

Method S.2

Preparation of alkyl (25-33), benzyl (34-39), allenyl (49-50), 2-thienylmethyl (54) and 3-thienylmethyl cobaloximes (55).

Above mentioned cobaloximes were prepared by the following general procedure.

This method is similar to Method S.1 except for the following modifications. After the formation of the $Co^{II}(dmgH)_2Py$ dimer, an aqueous solution of NaOH (1 mol equivalent) was added followed by solid sodium borohydride (0.5 mol equivalent). The addition of organic halide (1 mol equivalent) and the work up procedure was similar to the method S.1. The crystallisation of the product was done using a mixture of CH_2Cl_2:cyclohexane (2:1, v/v).

Method S.3

Preparation of propargyl cobaloxime (51)

Cobaloxime(I) was formed in situ by the reduction of chlorocobaloxime (7.36g, 20 mmol) as described under method S.2. The solvent used here was a mixture of dioxan (50 mL) and water (25 mL). Cobalt hydride was prepared by adding dilute acetic acid dropwise to the cobaloxime(I) till the pH became 8 as checked by standard pH paper. A solution of propargyl bromide (2.36g, 20 mmol) in dioxan-water (2:1) mixture (10 mL) was added to the above dark solution dropwise within 1 minute. After stirring for additional 5 min., the solution was poured into water (100 mL). The precipitated solid was filtered, washed with water and ether

and then dried in vacuo.

Method S.4

Preparation of 3-, 4-methoxy benzyl (40-41), methylene phenyl sulphide (42) and furfuryl (53) cobaloximes.

The following general method was employed for the synthesis:

Chlorocobaloxime (24) (7.36g, 20 mmol) was suspended under N_2 gas in methanol (150 mL) as described in method S.1. After stirring for 15 min a few drops of aqueous sodium hydroxide was added followed by solid $NaBH_4$ (1.51g, 40 mmol). A degassed solution of the appropriate halide (20 mmol) in methanol (10 mL) was added dropwise to the resulting blue cobaloxime(I) solution. The colour change from blue to red/orange was slower in case of tosylate than the halide. After stirring at room temperature, for some time (1.0 hr for halide and 8-10 hr for tosylate), the methanolic solution was concentrated in vacuo and the mixture was poured into water (200 mL). The precipitated cobaloxime was filtered immediately, washed with ether and dried in vacuo. The crude product was purified by flash chromatography using a mixture of CH_2Cl_2:CH_3OH:Py (90:9:1, v/v; 200 mL) as solvent. The eluent was concentrated in vacuo and the residual crystals were pumped free of solvent at room temperature.

2.2.3 Reaction of Organocobaloximes with organosulphenyl chlorides under different conditions.

The reactions have been carried out by the following general method.

Thermal Reactions (T)

Under anaerobic condition

A stream of nitrogen was passed for 15 minutes through dichloromethane solvent (30 ml) taken in a 50 ml two-necked RB flask. Organocobaloxime (2 mmol), organosulphenyl chloride (2.5 mmol) and pyridine (3 drops) were added successively. The mixture was heated to reflux on a water bath under a positive pressure of nitrogen. The reaction was monitored by TLC using ethyl acetate as eluent.

After completion of the reaction, the solution was concentrated (ca. 5 ml) in vacuo and was added dropwise into diethyl ether or petroleum ether 40-60^{o}C (50 ml). The precipitated inorganic product was filtered, washed with ether (3x25 ml), and dried under vacuo. The washings were mixed with the filtrate and solvent was removed under reduced pressure. The product was separated from crude mixture by preparative TLC using petroleum ether (60-80^{o}C) as eluent. The solid products were further recrystallised from petroleum ether (40-60^{o}C) as solids.

Photochemical Reactions Using 2x200 Watt Tungsten Lamp [P1].

The reactions were carried out in the specially designed all glass apparatus having external water-cooling system.

P1 Under anaerobic condition

Organocobaloxime (2 mmol) and organosulphenyl chloride (2.5-5.0 mmol) were added successively to degassed dichloromethane (50 ml). Two 200 W tungsten lamps were placed 5 cm apart from the reaction vessel and the solution was irradiated while cold water (5-10^{o}C) was circulated through the water jacket. The reaction

was monitored for cobaloxime by TLC on silica get using ethyl acetate as eluent.

After completion of the reaction the mixture was concentrated in vacuo and subjected directly to flash chromatography. The organic products were eluated out first by dichloromethane followed by the inorganic product, eluated by dichloromethane : acetone mixture (1:4). The crude organic mixture thus obtained was further subjected to gravity column chromatography using hexane as eluent. The solid products were recrystallized as described in method T.

Photochemical Reaction in Srinivasan's Photoreactor (400 W medium pressure UV-lamp) [P2]

P2 Under anaerobic condition

A solution of organocobaloxime (2 mmol) and benzene sulphenyl chloride (3 mmol) (5 drops) in dry chloroform (45 ml) was thoroughly degassed with nitrogen for 15 minutes. The mixture was transferred to quartz tubes (15 ml capacity) under nitrogen and were stoppered. The tubes were placed in the reactor and irradiated by a 400 W UV lamp placed inside a double walled quartz tube, through which ice cold water was circulated. After completion of the reaction the reaction mixture was worked up as detailed in method P1.

Dark Reactions

(a) The procedure was exactly similar to that described in P1, except that the reaction vessel was covered with the aluminium foil and the reaction was carried out in dark at $0^{o}C$. On completion the mixture was concentrated and poured into ether. The precipitated solid was filtered off and washed with ether.

The combined ether extract was concentrated and then chromatographed to obtain organic products which were characterized either directly by comparison with authentic sample or by conventional spectroscopic methods. The precipitated inorganic product was further purified on gravity column using a mixture of dichloromethane and ethylacetate. Inorganic products were identified mainly from their ^1H NMR spectra.

A_T In Acetic Acid

(b) The reactions in acetic acid were carried out exactly as above. However, the following modified work up procedure was employed. On completion, the inorganic product was filtered off and the filtrate was poured into water. The organic product was extracted with ether solvent and the organic layer was neutralized with sodium bicarbonate (conc. 5%), followed by water and sodium metabisulphite (5%). Dichloromethane extraction of the aqueous part gave more inorganic product. The ether layer, on evaporation, afforded organic product which was further separated and purified on the column using petroleum ether (60^oC-80^oC) as eluent.

Reaction in the presence of benzoyl peroxide/galvinoxyl

Benzoyl peroxide/galvinoxyl (ca. 5% w/w) was added to 30 ml dichloromethane containing organocobaloxime (2 mmol) and organosulphenyl chloride (25 mmol). The reaction was carried out as described above.

2.3 Results

2.3.1 Formation of Organocobaloximes (25-55)

The standard work-up procedures are followed for the isolation of organocobaloximes as outlined in the experimental section 2.2.2 p. 79 except for some special cases where some modifications are required, for example, 4-nitrobenzyl cobaloxime (39) requires immediate work-up after the addition of halide to $(Co^{I})^{-}$ since it has the tendency to decompose in solution. α-Pinenyl cobaloxime (48) is very unstable and is highly soluble in almost all organic solvents. It is advisable to carry out the work-up under nitrogen atmosphere, washing carefully with organic solvents and storing under nitrogen in the dark. In general, it is recommended that all the organocobaloximes should be stored under nitrogen atmosphere and are well covered by aluminium foil.

Cobaloxime synthesis is dominated by two approaches : the addition of hydrido cobaloxime to olefins and the alkylation of $(Co^{I})^{-}$ anions. The latter is more frequently used technique and involves 'in situ' generation of $(Co^{I})^{-}$. Its reaction with organic halides is visibly fast (by the colour change from blue to orange red).

Several mechanisms are known for the formation of organocobaloximes and the reaction of $(Co^{I})^{-}$ with substrate RX, may occur by any of these mechanisms depending upon whether RX is halide or tosylate, reaction conditions and reagents used. However, in the present studies two of the mechanisms, S_N2 [67,113] (eq. 81) and electron transfer [71,115,116] (eq. 82-84) require further discussion.

$$(Co^{I})^{-} + RX \longrightarrow R\text{-}(Co^{III}) + X^{-} \quad (81)$$

$$(Co^{I})^{-} + RX \longrightarrow (Co^{II}) + RX^{\dot{-}} \quad (82)$$

$$RX^{\dot{-}} \longrightarrow \dot{R} + X^{-} \quad (83)$$

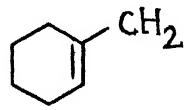
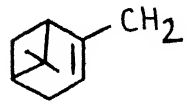
$$(Co^{II}) + \dot{R} \longrightarrow R\text{-}(Co^{III}) \quad (84)$$

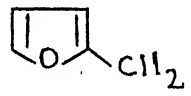
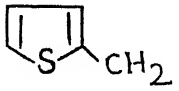
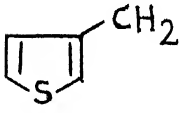
Extensive studies carried out by Schrauzer and coworkers[67] led to the earlier conclusion that the alkylation reaction, which is reversible, proceeds through an S_N2 mechanism. Later observations of inversion of configuration at the reacting carbon centre by Jenson et al[110-112] supported this view. However, they seemed to have missed the electron transfer component of such reactions, and attempts to demonstrate the expected inversion of configuration at carbon resulting from these oxidative additions led to such erroneous conclusions. It is now accepted that in the absence of exogeneous reducing agents, atom transfer process is the most likely process occurring in the formation of organocobaloximes. In this regard, Tada's[117-118] contribution is noteworthy who has given conclusive evidence in support of electron transfer mechanism. The details has been mentioned earlier in Chap. 1, page 18-20.

In the present study we have used only the organic halides and we believe that the reactions occur via electron transfer mechanism. All organocobaloximes described in this thesis are orange red solids, having similar chromatographic behaviour on silica gel plate. The typical R_f values in ethyl acetate are between 4-5 on a 10 point scale. The spectral characteristics of these organocobaloximes are given in table 2.1.

Table 2.1 Spectral Characteristics of Organocobaloximes, $RCo^{III}(dmgH)_2Py$ (24-55)

Compound No.	RCo^{III} R =	^1H NMR Chemical Shift δ(ppm), TMS($CDCl_3$) dmgH	R	Pyridine (β) (γ) (α)	UV VIS λ_{max}(nm) CH_3OH
1	2	3	4	5	6
(24)	Cl	2.35		7.26,7.73,8.25	468,360,275,233
(25)	CH_3^1	2.13	0.82(H1)	7.32,7.73,8.23	438,228
(26)	$CH_3^2CH_2^1$	2.15	1.75(H1),0.34(H2)	7.32,7.74,8.49	452,239
(27)	$CH_3^3CH_2^2CH_2^1$	2.12	1.63(H1),0.88(H2) 0.75(H3)	7.30,7.75,8.65	452,259
(28)	$(CH_3)_2^2CH^1$	2.12	2.12(H1),0.46(H2)	7.30,7.72,8.65	463,235
(29)	$CH_3^3(CH_2)_2^2CH_2^1$	2.12	1.66(H1),1.24(H2) 0.78(H3)	7.30,7.69,8.64	452,230
(30)	$CH_3^3(CH_2)_4^2CH_2^1$	2.11	1.65(H1),1.20(H2) 0.78(H3)	7.32,7.65,8.64	454,230
(31)	$PhCH_2^2CH_2^1$	2.10	1.69-1.9(H1,H2) 7.0-7.5(Ar)	7.0 - 7.5,8.60	464,240
(32)	$PhCH_2^3CH_2^2CH_2^1$	2.08	1.03-1.85(H1,H2) 2.53(H3), 7.1-7.4(Ar)	7.1-7.4,7.74,8.65	462,240
(33)	$PhO(CH_2)_2^2CH_2^1$	2.14	1.24-1.77(H1,H2) 3.84(H2), 6.76-7.50(Ar)	6.16-7.50,7.74,8.60	468,238
(34)	$PhCH_2^1$	1.90	2.80(H1),6.95(Ar)	7.30,7.73,8.40	455,352,272,238
(35)	$4\text{-}Me^2C_6H_4CH_2^1$	1.95	2.90(H1),2.36(H2) 6.90(Ar)	7.36,7.78,8.52	452,356,274,257

(36)	4-$Me^{2}_{3}CC_6H_4CH^{1}_{2}$	1.95	2.85(H1),1.25(H2) 7.08-7.15(Ar)	7.25, 7.70, 8.55	450,360,276,233
(37)	4-$ClC_6H_4CH^{1}_{2}$	2.00	2.73(H1),7.20(Ar)	7.30,7.80,8.56	455,363,370,240
(38)	4-$CNC_6H_4CH^{1}_{2}$	1.98	2.71(H1), 6.90-7.30(Ar)	7.25,7.70,8.50	460,340,277,237
(39)	4-$NO_2C_6H_4CH^{1}_{2}$	2.06	3.35(H1) 6.86-7.54(Ar)	7.72,8.22,8.76	445,350,300,235
(40)	4-$Me^{2}OC_6H_4CH^{1}_{2}$	1.95	2.85(H1),2.75(H2) 6.60-6.90(Ar)	7.25,7.68,8.55	448,380,287,232
(41)	3-$Me^{2}OC_6H_4CH^{1}_{2}$	2.10	2.90(H1),3.88(H2) 6.50-7.00(Ar)	7.20,7.60,8.44	457,352,270,232
(42)	$PhSCH^{1}_{2}$	2.00	3.10(H1) 6.98-7.63(Ar)	7.74,8.10,8.52	460,348,273,239
(43)	$CH^{3}_{2}=CH^{2}-CH^{1}_{2}$	2.35	3.80(H1),5.65(H2) 5.35(H3)	7.30,7.70,8.50	458,348,232
(44)	$Me^{4}CH^{3}=CH^{2}-CH^{1}_{2}$	2.20	2.40(H1),5.50(H2), 5.50(H3),1.25(H4)	7.30,7.70,8.60	457,348,273,238
(45)	$Me^{3}_{2}C=CH^{2}-CH^{1}_{2}$	2.05	2.40(H1),5.00(H2) 1.10-1.20(H3)	7.20,7.50,8.50	457,348,270,220
(46)	$PhCH^{3}=CH^{2}-CH^{1}_{2}$	2.12	2.51(H1),4.98(H2), 6.16(H3),7.20(Ar)	7.20,7.60,8.50	458,350,250,227
(47)		2.14	2.48(H1),5.28(H2), 1.42-2.78(H3)	7.30,7.70,8.57	467,380,350,285
(48)		2.12	2.31(H1),5.40(H2), 1.42-2.78(H3) 0.72, 1.24(gem Me)	7.30,7.63,8.61	485,465,409,34 311,241

(49)	$CH_2^2=C=CH^1$	2.20	4.95(H1),4.50(H2)	7.30,7.75,8.50	462,240
(50)	$Me_2^2C=C=CH^1$	2.10	4.75(H1),1.20(H2)	7.30,7.60,8.60	455,373,366,332, 288,235
(51)	$H^2C\equiv C-CH_2^1$	2.22	2.30(H1),2.30(H2)	7.35-8.65	463,355,230
(52)	$CH_2^4=CH^3-CH_2^2-CH_2^1$	2.10	1.62(H1),(H2,H3)* 4.80(H4)	7.18,7.56,8.52	450,380,290,232
(53)		2.10	2.40(H1), 6.00-7.40(Ar)	7.30,7.75,8.60	363,284,239
(54)		2.05	3.00(H1) 6.65-7.00(Ar)	7.20,7.65,8.50	385,281,240
(55)		2.00 2.10	2.85(H1) 6.65-7.20(Ar)	7.30,7.70,8.00	359,277,239

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*Resonance obscured

2.4 Reaction of Alkyl (25-33), benzyl (34-42), heteroaromatic methyl (53-55), allyl (43-48) and other organocobaloximes (49-52) with arene sulphenyl chloride (A, B and C).

2.4.1 Results

Alkyl cobaloximes (25-33) react with benzene sulphenyl chloride (A) in 1:1.1 molar ratio under P1 conditions to give the corresponding alkyl phenyl sulphides in 50-70% yield. The reaction is slow and takes 4-20 h depending upon the substrate cobaloxime. The reaction time is drastically reduced under P2 conditions, however, the yield and the nature of the products remain the same. Similar observations are made in the reactions of these organocobaloximes with pentachlorobenzene sulphenyl chloride (B) and 2,4 dinitrobenzene sulphenyl chloride (C). In general, it is found that the yields are best obtained with pentachlorobenzene sulphenyl chloride (B). Similarly, the reaction time is drastically reduced under P2 conditions. The inorganic product in all cases is chlorocobaloxime (24) (see table 2.2 and 2.3).

Benzyl and substituted benzyl cobaloximes (34-42) react with (A) or (B) under P1 or P2 conditions and in 1:1.1 molar ratio to give the corresponding benzyl sulphides. The reaction under thermal conditions are slow for example, the reaction of (34) with (B) under thermal conditions remains incomplete even after 40 h at room temperature under dark and the only organic product isolated is the corresponding benzyl sulphide (78). 3-Methoxybenzyl cobaloxime (41) forms the corresponding sulphide (98) under P1 conditions whereas under dark conditions it forms the ring

$$RCo^{III} \text{ (25-33)} + ArSCl \xrightarrow{h\nu} RSAr \text{ (56-76)} + ClCo^{III} \text{ (24)}$$

Table 2.2 Organic Products from the reaction of RCo^{III} [25-33] with arenesulphenyl halides [A,B and C]*

RCo^{III}, R= (Comp.no.)	Organic precursor	Reaction Condition time(h)	Organic products (product no.)	Yield (%)
(25)CH_3	(A)	P1/20	$CH_3SC_6H_5$, (56)	50
		P2/2	$CH_3SC_6H_5$, (56)	50
	(B)	P1/20	$CH_3SC_6Cl_5$, (57)	88
		P2/6	$CH_3SC_6Cl_5$, (57)	85
	(C)	P1/16	$CH_3SC_6H_3(NO_2)_2$, (58)	50
		P2/4	$CH_3SC_6H_3(NO_2)_2$, (58)	55
(26)CH_3CH_2	(A)	P1/14	$CH_3CH_2SC_6H_5$, (59)	55
		P2/1	$CH_3CH_2SC_6H_5$, (59)	50
	(B)	P1/15	$CH_3CH_2SC_6Cl_5$, (60)	91
		P2/6	$CH_3CH_2SC_6Cl_5$, (60)	84
	(C)	P1/12	$CH_3CH_2SC_6H_3(NO_2)_2$, (61)	60
		P2/2	$CH_3CH_2SC_6H_3(NO_2)_2$, (61)	62
(27)$CH_3CH_2CH_2$	(A)	P1/8	$CH_3CH_2CH_2SC_6H_5$, (62)	64
		P1/0.5	$CH_3CH_2CH_2SC_6H_5$, (62)	60
	(B)	P1/6	$CH_3CH_2CH_2SC_6Cl_5$, (63)	94
		P2/0.75	$CH_3CH_2CH_2SC_6Cl_5$, (63)	90
	(C)	P1/7	$CH_3CH_2CH_2SC_6H_3(NO_2)_2$, (64)	64
		P2/0.75	$CH_3CH_2CH_2SC_6H_3(NO_2)_2$, (64)	65

(28)$(CH_3)_2CH$	(A)	P1/5	$(CH_3)_2CHSC_6H_5$, (65)	70
		P2/0.5	$(CH_3)_2CHSC_6H_5$, (65)	68
	(B)	P1/5.5	$(CH_3)_2CHSC_6Cl_5$, (66)	92
		P2/0.64	$(CH_3)_2CHSC_6Cl_5$, (66)	90
	(C)	P1/6	$(CH_3)_2CHSC_6H_3(NO_2)_2$, (67)	66
		P2/0.75	$(CH_3)_2CHSC_6H_3(NO_2)_2$, (67)	68
(29)$CH_3(CH_2)_2CH_2$	(A)	P1/11	$CH_3(CH_2)_2CH_2SC_6H_5$, (68)	68
		P2/0.8	$CH_3(CH_2)_2CH_2SC_6H_5$, (68)	65
	(B)	P1/9	$CH_3(CH_2)_2CH_2SC_6Cl_5$, (69)	90
		P2/0.75	$CH_3(CH_2)_2CH_2SC_6Cl_5$, (69)	86
	(C)	P1/8	$CH_3(CH_2)_2CH_2SC_6H_3(NO_2)_2$, (70)	60
		P2/1	$CH_3(CH_2)_2CH_2SC_6H_3(NO_2)_2$, (70)	60
(30)$CH_3(CH_2)_4CH_2$	(A)	P1/14	$CH_3(CH_2)_4CH_2SC_6H_5$, (71)	65
		P2/0.8	$CH_3(CH_2)_4CH_2SC_6H_5$, (71)	64
	(B)	P1/8.5	$CH_3(CH_2)_4CH_2SC_6Cl_5$, (72)	88
		P2/1	$CH_3(CH_2)_4CH_2SC_6Cl_5$, (72)	80
	(C)	P1/9	$CH_3(CH_2)_4CH_2SC_6H_3(NO_2)_2$, (73)	58
		P2/1	$CH_3(CH_2)_4CH_2SC_6H_3(NO_2)_2$, (73)	60
(31)$PhCH_2CH_2$	(B)	P1/6.5	$PhCH_2CH_2SC_6Cl_5$, (74)	87
(32)$PhCH_2CH_2CH_2$	(B)	P1/7	$PhCH_2CH_2CH_2SC_6Cl_5$, (75)	84
(33)$PhOCH_2CH_2CH_2$	(B)	P1/4	$PhOCH_2CH_2CH_2SC_6Cl_5$, (76)	81

*[(A) = C_6H_5SCl, (B) = C_6Cl_5SCl and (C) = $2,4\text{-}(NO_2)_2C_6H_3SCl$

Table 2.3 : Characteristics of alkyl sulphides (56-76)

Product No.	^{1}H NMR Chemical Shift δ(ppm), (multiplicity) $-CH_2S-$	$(CH_2)_n$	CH_3	Aromatic	M.P. (^oC)	UV-VIS λ_{max}(nm) (CH_3OH)
1	2	3	4	5	6	7
(56)	2.33(s)	-	-	7.02(s)	liq.	280, 254, 225
(57)	2.33(s)	-	-	-	65	295, 214
(58)	2.35(s)	-	-	7.31(s),7.48(s) 8.1(d),8.25(d) 8.78(d)	126	335, 270, 210
(59)	2.84(q)	-	2.33(t)	7.01(s)	liq.	290, 258, 220
(60)	2.9(q)	-	2.33(t)	-	66	296, 214
(61)	3.0(q)	-	2.36(t)	7.32(s),7.48(s) 8.2(d) ,8.24(d) 8.78(d)	88	335, 270, 211
(62)	2.75(t)	1.6(m)	1.06(t)	7.02(s)	liq.	290, 259, 220
(63)	2.83(t)	1.5(m)	1.0(t)	-	59	297, 213.5
(64)	2.8(t)	1.7(m)	1.16(t)	7.32(s),7.48(s) 8.1(d) ,8.26(d) 8.8(d)	80	335, 272, 210
(65)	3.25(m)	-	1.3(d)	7.2(s)	liq.	310, 258, 225
(66)	3.46(m)	-	1.23(d)	-	55	298, 213.5
(67)	3.56(m)	-	1.5(d)	7.4(s),7.6(s) 8.2(d),8.35(d) 8.85(d)	95	336, 271, 211
(68)	2.84(t)	1.5(bm)	0.7(bm)	7.1(m)	liq.	326, 249, 220.5
(69)	2.9(t)	1.5(bm)	0.97(bm)	-	72	296.5, 213
(70)	2.8(t)	1.55(bm)	0.82(bm)	7.25(s),7.44(s) 8.1(d),8.26(d) 8.78(d)	65	335, 272, 210
(71)	2.85(t)	1.5(bm)	0.8(bm)	7.2(m)	liq.	310, 252, 222

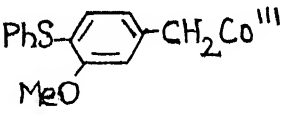
(72)	2.8(t)	1.5(bm)	0.86(bm)	-	76	300, 217.5
(73)	2.85(t)	1.6(bm)	0.8 (bm)	7.26(s),7.46(s) 8.1(d),8.25(d) 8.78(d)	74	336, 270, 221
(74)	2.6-3.3(m)	2.6-3.3(m)	-	7.03	64	297, 220
(75)	2.5-3.0(m)	1.6-2.1(m)	2.5-2.9(m)	6.5-7.4(m)	65	290, 222
(76)	3.0-3.3(t)	1.8-2.2(m)	3.6-4.3(t)	6.5-7.2(m)	60	284, 219

RCo^{III} (34-42) + ArSCl (A,B,C) $\xrightarrow{h\nu \text{ or } \Delta}$ RSAr (77-100) + RR (101-107) + RdmgH (108-114)

Table 2.4 Organic Products from the reaction of RCo^{III} [34-42] with arenesulphenyl halides [A,B and C]*

RCo^{III}, R = (Comp. no.)	Organic precursor	Reaction Condition time (h)	Organic products (product no.)	Yields (%)
(34)$C_6H_5CH_2$	(A)	P1/5	$C_6H_5CH_2SC_6H_5$, (77)	58
		P2/1	$C_6H_5CH_2SC_6H_5$, (77)	50
	(B)	P1/6	$C_6H_5CH_2SC_6Cl_5$, (78)	72
		P2/3.5	$C_6H_5CH_2SC_6Cl_5$, (78)	81
		T/7.5	$C_6H_5CH_2SC_6Cl_5$, (78)	65
		RT/dark/40	$C_6H_5CH_2SC_6Cl_5$, (78)	incomplete
	(C)	P1/0.8	$C_6H_5CH_2SC_6H_3(NO_2)_2$, (79)	50
			$(C_6H_5CH_2)_2$, (101)	15
		T/6.6	$C_6H_5CH_2SC_6H_3(NO_2)_2$, (79)	54
			$C_6H_5CH_2$dmgH, (108)	18
(35)4-$MeC_6H_4CH_2$	(A)	P1/4	4-$MeC_6H_4CH_2SC_6H_5$, (80)	64
		P2/0.75	4-$MeC_6H_4CH_2SC_6H_5$, (80)	62
	(B)	P1/3.5	4-$MeC_6H_4CH_2SC_6Cl_5$, (81)	70
		P2/1	4-$MeC_6H_4CH_2SC_6Cl_5$, (81)	75
	(C)	P1/0.75	4-$MeC_6H_4CH_2SC_6H_3(NO_2)_2$, (82)	60
			$(4\text{-}MeC_6H_4CH_2)_2$, (102)	20
		T/5	4-$MeC_6H_4CH_2SC_6H_3(NO_2)_2$, (82)	70
			4-$MeC_6H_4CH_2$dmgH, (109)	10

(36) 4-$Me_3CC_6H_4CH_2$	(A)	P1/4.5	4-$Me_3CC_6H_4CH_2SC_6H_5$, (83)	60
		P2/1	4-$Me_3CC_6H_4CH_2SC_6H_5$, (83)	58
	(B)	P1/3	4-$Me_3CC_6H_4CH_2SC_6Cl_5$, (84)	69
		P2/1	4-$Me_3CC_6H_4CH_2SC_6Cl_5$, (84)	76
	(C)	P1/1.5	4-$Me_3CC_6H_4CH_2SC_6H_3(NO_2)_2$, (85)	60
			$(4\text{-}Me_3CC_6H_4CH_2)_2$, (103)	18
		T/4	4-$Me_3CC_6H_4CH_2SC_6H_3(NO_2)_2$, (85)	62
			4-$Me_3CC_6H_4CH_2$dmgH, (110)	17
(37) 4-$ClC_6H_4CH_2$	(A)	P1/2.5	4-$ClC_6H_4CH_2SC_6H_5$, (86)	60
		P2/1	4-$ClC_6H_4CH_2SC_6H_5$, (86)	58
	(B)	P1/6.5	4-$ClC_6H_4CH_2SC_6Cl_5$, (87)	74
		P2/1.5	4-$ClC_6H_4CH_2SC_6Cl_5$, (87)	76
	(C)	P1/1.5	4-$ClC_6H_4CH_2SC_6H_3(NO_2)_2$, (88)	55
			$(4\text{-}ClC_6H_4CH_2)_2$, (104)	26
		T/5.5	4-$ClC_6H_4CH_2SC_6H_3(NO_2)_2$, (88)	66
			4-$ClC_6H_4CH_2$dmgH, (111)	15
(38) 4-$CNC_6H_4CH_2$	(A)	P1/3.5	4-$CNC_6H_4CH_2SC_6H_5$, (89)	45
		P2/1	4-$CNC_6H_4CH_2SC_6H_5$, (89)	44
	(B)	P1/5.5	4-$CNC_6H_4CH_2SC_6Cl_5$, (90)	68
		P2/1.15	4-$CNC_6H_4CH_2SC_6Cl_5$, (90)	71
	(C)	P1/2.5	4-$CNC_6H_4CH_2SC_6H_3(NO_2)_2$, (91)	55
			$(4\text{-}CNC_6H_4CH_2)_2$, (105)	20
		T/5	4-$CNC_6H_4CH_2SC_6H_3(NO_2)_2$, (91)	58
			4-$CNC_6H_4CH_2$dmgH, (112)	10

(39)4-$NO_2C_6H_4CH_2$	(A)	P1/2.5	4-$NO_2C_6H_4CH_2SC_6H_5$, (92)	48
		P2/1	4-$NO_2C_6H_4CH_2SC_6H_5$, (92)	45
	(B)	P1/5	4-$NO_2C_6H_4CH_2SC_6Cl_5$, (93)	67
		P2/1.15	4-$NO_2C_6H_4CH_2SC_6Cl_5$, (93)	72
	(C)	P1/3.5	4-$NO_2C_6H_4CH_2SC_6H_3(NO_2)_2$, (94)	50
			$(4\text{-}NO_2C_6H_4CH_2)_2$, (106)	18
		T/6	4-$NO_2C_6H_4CH_2SC_6H_3(NO_2)_2$, (94)	52
			4-$NO_2C_6H_4CH_2$dmgH, (113)	15
(40)4-$MeOC_6H_4CH_2$**	(A)	P1/4	4-$MeOC_6H_4CH_2SC_6H_5$, (95)	64
		P2/0.75	4-$MeOC_6H_4CH_2SC_6H_5$, (95)	60
	(B)	P1/3	4-$MeOC_6H_4CH_2SC_6Cl_5$, (96)	68
		P2/1	4-$MeOC_6H_4CH_2SC_6Cl_5$, (96)	74
	(C)	P1/0.8	4-$MeOC_6H_4CH_2SC_6H_3(NO_2)_2$, (97)	62
			$(4\text{-}MeOC_6H_4CH_2)_2$, (107)	18
		T/3.5	4-$MeOC_6H_4CH_2SC_6H_3(NO_2)_2$, (97)	68
			4-$MeOC_6H_4CH_2$dmgH, (114)	10
(41) 3-$MeOC_6H_4CH_2$	(A)	P1/14	3-$MeOC_6H_4CH_2SC_6H_5$, (98)	32
		dark/0°C/10 (incomplete)	 (99)	40
(42)$C_6H_5SCH_2$	(B)	P1/4	$C_6H_5SCH_2SC_6Cl_5$, (100)	62

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* [(A) = C_6H_5SCl, (B) = C_6Cl_5SCl and (C) = 2,4-$(NO_2)_2C_6H_3SCl$]

** The reaction of (40) with (A) under dark at 0°C is not clean and forms a mixture of organic products.

Table 2.5 : Characteristics of benzyl sulphides (77-100)

Product No.	^{1}H NMR Chemical Shift δ(ppm),(multiplicity) $-CH_2S-$*	Aromatic	Others*	M.P. (°C)	UV-VIS λ_{max}(nm) (CH_3OH)
1	2	3	4	5	6
(77)	4.0	7.25(s)	-	40	266,228
(78)	4.05	7.13(s)	-	75	237,217.5
(79)	4.3	7.4(s),7.43(s) 8.31(d),8.4(d) 9.1(d)	-	130	332,269
(80)	4.0	7.06(s)	2.22	70	264,231
(81)	4.06	7.03(s)	2.25	76	237, 216
(82)	4.2	7.2(s),7.5(s) 7.6(s),8.25(d) 8.35(d),9.1(d)	2.3	121	334,270,230
(83)	3.9	7.01-7.28(m)	1.2	50	259,252,219
(84)	4.06	7.03-7.36(m)	1.27	73	268,213
(85)	4.2	7.0-7.2(m),7.5(s) 7.6(s),8.25(d) 8.35(d),9.1(d)	1.32	122	335,270,230
(86)	3.95	7.16(s)	-	65	267,223
(87)	4.05	7.13(s)	-	114	263,217
(88)	4.15	7.1(s),7.34(s) 7.55(s),8.1(d) 8.9(d)	-	124	332,265,221
(89)	3.95	7.08(s),7.15-7.55(dd)	-	60	234,219
(90)	4.08	7.2-7.44(dd)	-	145	221,217
(91)	4.6	7.74-7.5(dd),7.9(s) 8.0(s),8.5(d) 8.6(d),9.12(d)	-	128	334,265,233
(92)	4.0	7.06(dd),7.15-7.88(d)	-	70	268,242,219
(93)	4.15	7.29-8.04(dd)	-	135	262,215

(94)	4.68	7.65-8.25(dd),7.87(s) 8.0(s),8.59(d) 8.71(d),9.15(d)	-	138	335,278,211
(95)	3.86	7.1,6.5-7.0(dd)	3.7	75	265,231
(96)	4.03	6.68-7.06(dd)	3.73	152	225,216
(97)	4.3	6.9-7.38(dd),7.68(s) 7.78(s),8.3(d),8.4(d) 9.1(d)	3.8	125	335,272,230
(98)	3.9	6.66-7.18(m)	3.6	120	338,272,228
(99)	a				
(100)	4.3	7.28(s)	-	88	217.5

* All signals appear as singlets.

a: ^{1}H NMR ($CDCl_3$) δ(ppm) : 1.98 (s, 12H, CH_3); 2.98 (s, 2H, CH_2) 3.72 (s, 3H, OCH_3); 6.6-7.2 (m, aromatic, pyridine); 7.48, 8.4 (m, pyridine); λ_{max} [MeOH] : 344, 246, 212.

Table 2.6 Characteristics of bibenzyls RR (101-107)

Compound No.	Compound	M.P. (^{o}C)	^{1}H NMR Chemical shift δ(ppm) Aromatic	CH_2
(101)	$C_6H_5CH_2CH_2C_6H_5$	51	7.1-7.4(m)	2.9(s)
(102)	4-$MeC_6H_4CH_2CH_2C_6H_4Me$-4	75	7.08(s)	2.86*(s)
(103)	4-$Me_3CC_6H_4CH_2CH_2C_6H_4CCMe_3$-4	82	7.09(s)	2.84$^{\#}$(s)
(104)	4-$ClC_6H_4CH_2CH_2C_6H_4Cl$-4	98	7.02,7.24^{a} (9 Hz)	2.84(s)
(105)	4-$CNC_6H_4CH_2CH_2C_6H_4CN$-4	198	7.16,7.94	2.86(s)
(106)	4-$NO_2C_6H_4CH_2CH_2C_6H_4NO_2$-4	180	7.23,8.1 (9 Hz)	3.08(s)
(107)	4-$MeOC_6H_4CH_2CH_2C_6H_4MeO_2$-4	80	7.02,7.66^{a} (11 Hz)	2.98(s)

*(CH_3 δ 2.3); $^{\#}$(CMe_3 δ 2.25)

a : A_2B_2 pattern is clearly observed and coupling constant is given in parentheses.

Table 2.7 Characteristics of Benzyl ethers of dimethylglyoxime, RdmgH (108-114)

Product No.	M.P. (°C)	^{1}H NMR Chemical shift δ(ppm) dmgH	$-CH_2$	Aromatic	UV-VIS λ_{max}(nm) CH_3(OH)	Mass (m+e)$
(108)	90-92	1.95	5.10	7.23	-	-
(109)	85	2.00,2.08	5.12	7.16	228	220(2%), 115(100%)
(110)	-	2.06,2.10	5.12	6.96,7.1	228	-
(111)	98	1.90,230	5.16	7.20	226	239(1.5%), 124(100%
(112)	95	1.95,2.04	5.16	7.40,7.52	235	231(10%), 116(100%)
(113)	99	A 2.05,2.35 B 2.18,2.22	5.35,5.10	7.59,8.20 7.50,8.20	217,230, 260	250(60%), 135(100%), 250(60%), 135(100%),
(114)	71	A 2.05,2.10 B 2.18,2.22	5.0,4.35	7.15,6.70	231,	236(12%), 121(50%),

* (OCH_3 δ 3.8)

$ values refer to $[M^+]$, $[M\text{-dmgH}]^+$ but for (111 and 113) the values $[M\text{-H}]^+$ and $[M\text{-H-dmgH}]^+$

Table 2.7 Characteristics of Benzyl ethers of dimethylglyoxime, RdmgH (108-114)

Product No.	M.P. (°C)	^{1}H NMR Chemical shift δ(ppm) dmgH	$-CH_2$	Aromatic	UV-VIS λ_{max}(nm) CH_3(OH)	Mass (m+e)$
(108)	90-92	1.95	5.10	7.23	-	-
(109)	85	2.00,2.08	5.12	7.16	228	220(2%), 115(100%)
(110)	-	2.06,2.10	5.12	6.96,7.1	228	-
(111)	98	1.90,230	5.16	7.20	226	239(1.5%),124(100%)
(112)	95	1.95,2.04	5.16	7.40,7.52	235	231(10%),116(100%)
(113)	99	A 2.05,2.35 B 2.18,2.22	5.35,5.10	7.59,8.20 7.50,8.20	217,230, 260	250(60%),135(100%), 250(60%),135(100%),
(114)	71	A 2.05,2.10 B 2.18,2.22	5.0,4.35	7.15,6.70	231,	236(12%),121(50%),

* (OCH_3 δ 3.8)

$ values refer to $[M^+]$, $[M-dmgH]^+$ but for (111 and 113) the values $[M-H]^+$ and $[M-H-dmgH]^+$

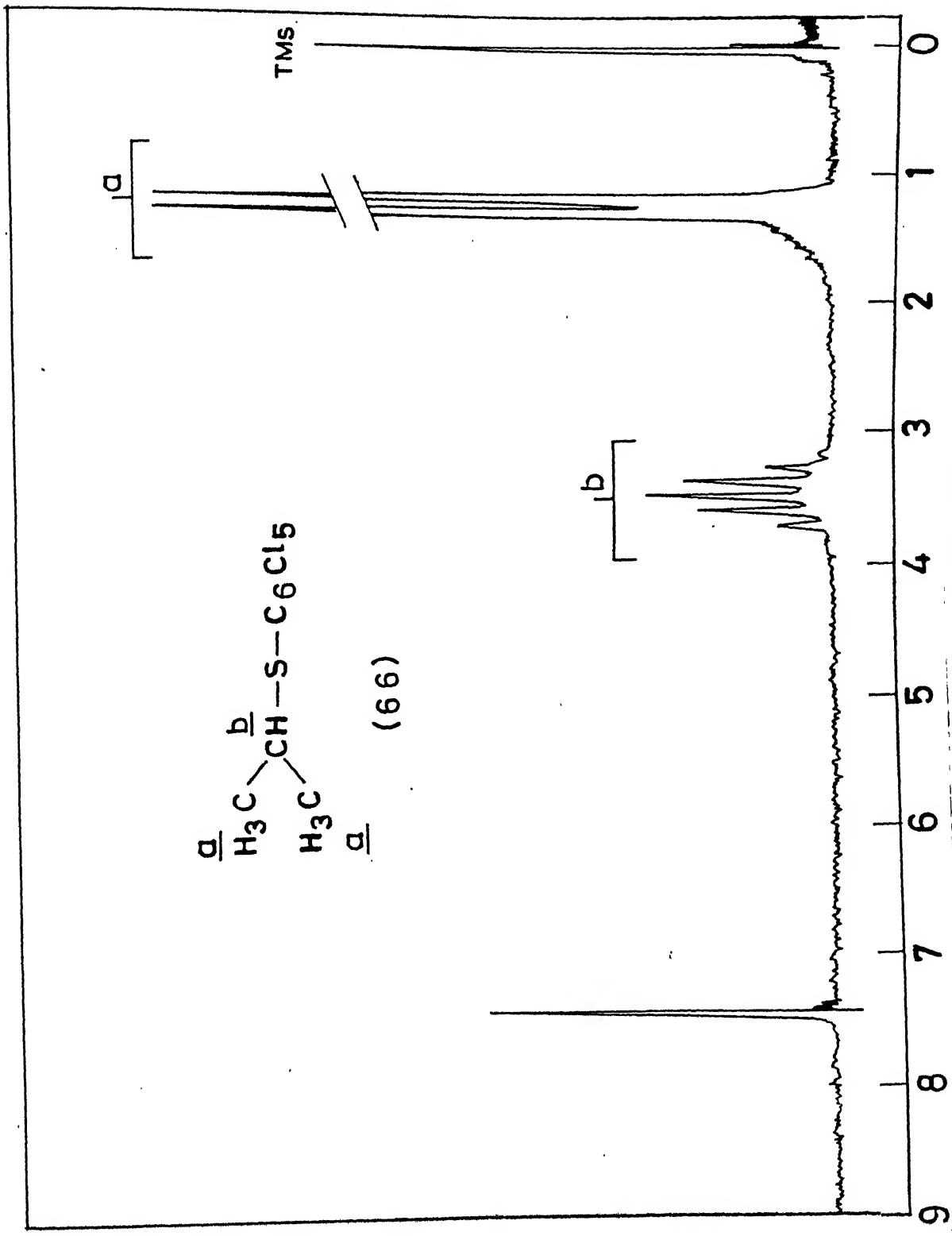
Table 2.8 Mass spectra of organic products from the reaction of alkyl (25-30) and benzyl (34-41) cobaloximes with ArSCl (A,B and C)

Sl.No.	Compound No.	Mass (m/e)	
1.	57[a]	296 (2.8%)	
2.	60[a]	310 (3.05%)	
3.	63[a]	324 (4.36%)	43 (100%)
4.	66[a]	324 (3.0%)	43 (88%)
5.	69[a]	338 (2.7%)	57 (100%)
6.	72[a]	366 (4.4%)	85 (100%)
7.	78[a]	372 (3.55%)	91 (100%)
8.	81[b]	385 (6.19%)	281 (8.7%), 105 (100%)
9.	84[c]	428 (11.7%)	147 (100%)
10.	87[a]	407 (4.2%)	126 (100%)
11.	90[b]	396 (1.52%)	117 (100%)
12.	93[b]	416 (12.45%)	136 (100%)
13.	96[b]	401 (0.5%)	117 (100%)

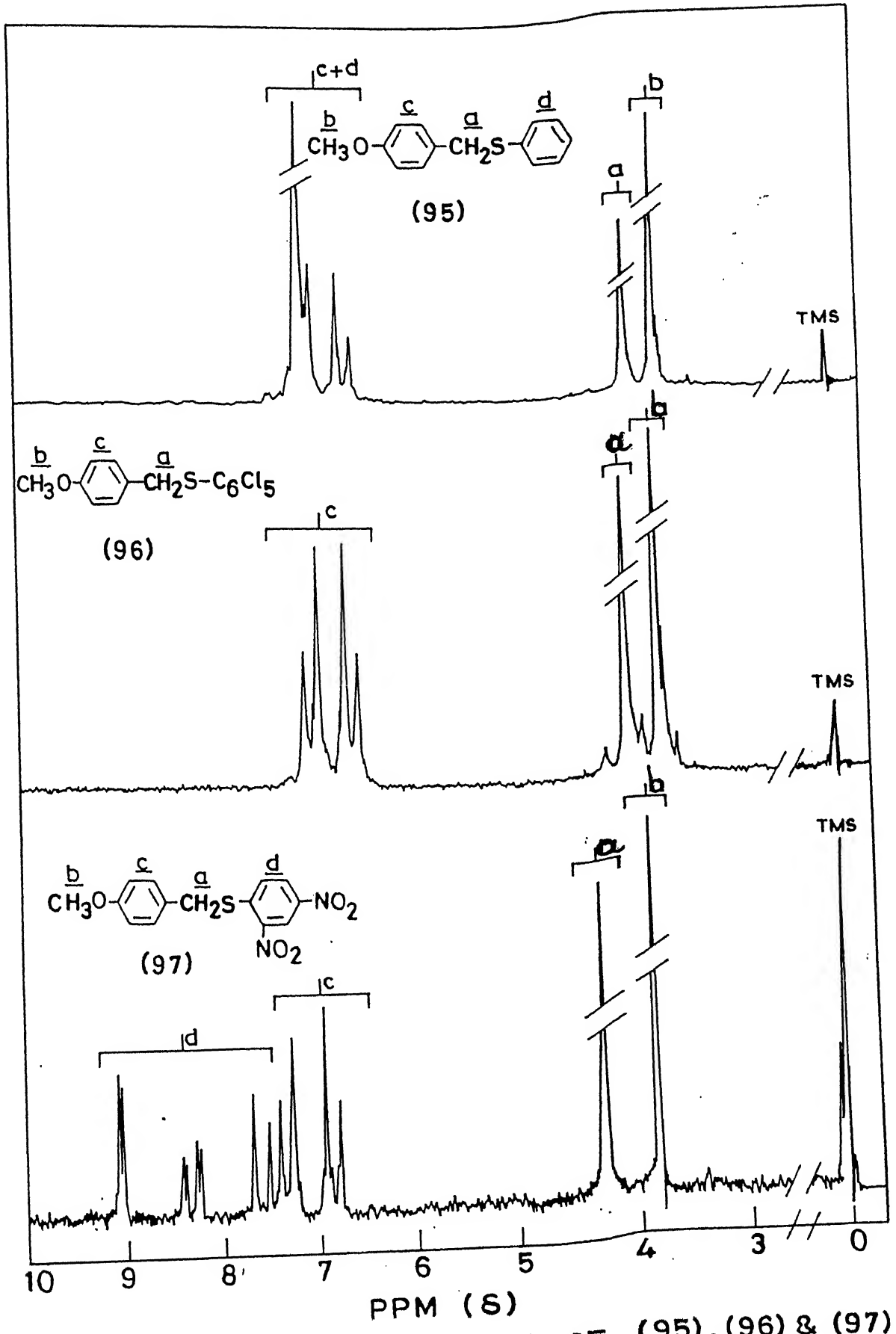
[a] values refer to (M^++2) and ($M-SC_6Cl_5$)

[b] values refer to (M^++H) and ($M-SC_6Cl_5$)

[c] values refer to (M^+) and ($M-SC_6Cl_5$)



^1H NMR SPECTRA (60 MHz) OF (66)



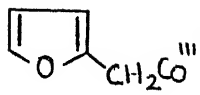
^1H NMR SPECTRA (60MHz) OF (95), (96) & (97)

substituted organometallic product (99). The reactions of benzyl cobaloximes (34-40) with (C) give different products under thermal (T) and photochemical conditions (P1), for example under P1 conditions the dimers (101-107) are formed along with the corresponding benzyl sulphides, whereas benzylic ethers of dimethylglyoximes (108-114) are formed along with the benzyl sulphides under thermal conditions (see table 2.4 to 2.7).

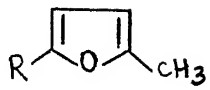
The reaction of heteroaromatic methyl cobaloximes (53-55) with A, B or C are, in general, faster compared to the benzyl cobaloximes and are finished within 1.5 h under all conditions, whether thermal or photochemical. Both organic and organometallic products are formed in each case (Scheme 2.3 and table 2.9). However, ring substituted organometallic product is the only product isolated in the reactions carried out at $0^{o}C$ under dark. The change in solvent from dichloromethane to acetic acid does not make any significant change in the nature of the products, however, the proportions of the products formed are different.

In general, all three heteroaromatic methyl cobaloximes (53-55) show a similar reactivity towards (A), (B) and (C) but few differences are noteworthy, i) the hydrocarbon product (115a-c) is formed in (53) but not in (54) and (55), ii) the ring substituted sulphides (116a-b, 120a-b, 124a-b) and monoethers (118a-b, 122a-b and 126a-b) are formed in the reaction with (A) and (B) but not with (C). The latter forms similar but unsubstituted ring products (116c, 118c, 120c, 122c, 124c and 126c).

The details of the products and their characteristics are given in Scheme 2.3 and tables 2.9-2.13.



(53)

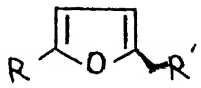


(115)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

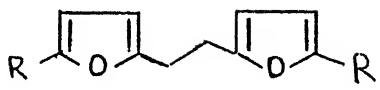


(116)

(a) R = R' = SC_6H_5

(b) R = R' = SC_6Cl_5

(c) R = H, R' = $SC_6H_3(NO_2)_2$

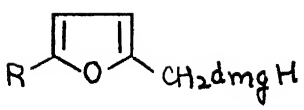


(117)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

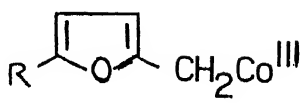


(118)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = H



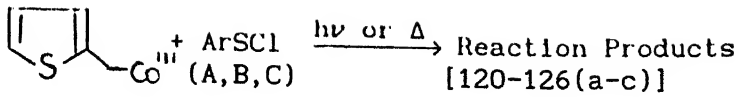
(119)

(a) R = SC_6H_5

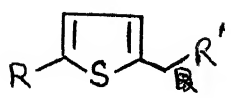
(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

Scheme 2.3



(54)

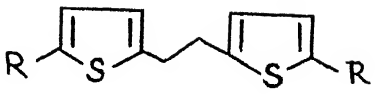


(120)

(a) R = R' = SC_6H_5

(b) R = R' = SC_6Cl_5

(c) R = H, R' = $SC_6H_3(NO_2)_2$

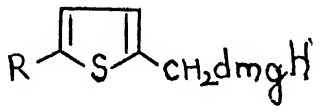


(121)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

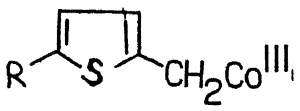


(122)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = H



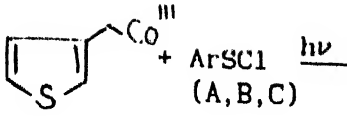
(123)

(a) R = SC_6H_5

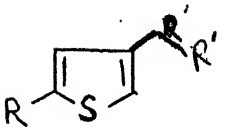
(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

Scheme 2.3 (contd.)



(55)

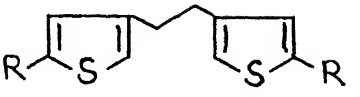


(124)

(a) R = R' = SC_6H_5

(b) R = R' = SC_6Cl_5

(c) R = H, R' = $SC_6H_3(NO_2)_2$

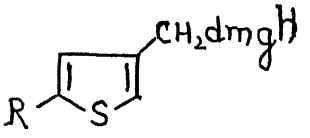


(125)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

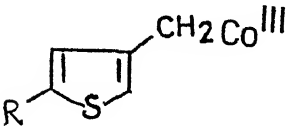


(126)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = H



(127)

(a) R = SC_6H_5

(b) R = SC_6Cl_5

(c) R = $SC_6H_3(NO_2)_2$

Scheme 2.3 (contd.)

Table 2.9 : Products of the Reaction of heteroaromatic methyl cobaloximes (53-55) with Arene sulphenyl chlorides (A),(B) and (C).

RCo(III)	Organic Precursor	Reaction Conditions time (h)	Organic/ Organometallic Products	Yield (%)
53	A	P1/0.6	115a	20
			116a	25
			117a	18
			118a	15
		$0^{o}C$ dark/1	119a	64
53	B	P1/0.6	115b	35
			116b	15
			117b**	10
			118b**	5
			119b	27
		$0^{o}C$ dark/1	115b	8
			116b	10
			118b**	15
			119b	60
		*P1/0.6	115b	10
			116b	27
			118b**	20
		**$A_T(0^{o}C)$/0.5	115b	35
			116b	26
			118b**	22
			119b	27

		**A_T(60°C)/0.6	115b	18
			116b	25
			118b**	28
	C	P1/0.35	115c	16
			116c	57
			117c	5
		0°C, dark/1	119c	40
		T/$CHCl_3$/0.75	115c	40
			118c	15
		**AcOH(RT)/1	115c	28
			118c	15
			119c	25
54	A	P1/1.5	120a	40
			121a	24
			122a	25
		0°C dark/0.5	123a	34
	B	P1/0.6	120b	18
			121b**	16
			123b	29
			119b	27
		0°C dark/1	123b	70
		A_T(0°C)/0.5	120b	30
			123b	26
	C	P1/0.8	120c	58
			121c	5
		0°C, dark/incomp	123c	18

		$T/CHCl_3/0.8$	120c	47
			122c	25
			123c	10
		AcOH(RT)/1.25	120c	28
			122c	26
55	A	P1/1.08	124a	38
			125a	27
			126a	19
		$0^{\circ}C$ dark/0.5	127a	30
	B	P1/2	124b	24
			125b**	16
			126b**	10
			127b	28
		$0^{\circ}C$ dark/1	127b	58
		*P1/5	124b	28
	C	P1/1.5	124c	58
			125c	5
		$0^{\circ}C$, dark/incomp	127c	17
		$CHCl_3/T/1.15$	124c	42
			126c	18
			127c	28

* Organometallic : ArSCl (1:3)

** The yield of organic products are based on the ^1H NMR integration only. The isolation is ≥ 90%.

Table 2.10 : Characteristics of Organic Products (115a-c—126a-c)

Organic Products	^{1}H NMR (Chemical shift, δ) CH_2	Heteroaromatic	Aromatic	Others	UV-VIS λ_{max}(nm) (CH_3OH)	MP(°C)
115a	-	5.92-6.41(dd)	7.0-7.1(m)	2.15(s)	242,209	84
115b	-	5.83-6.5(dd)	-	2.25(s)	221	114
115c	-	6.1-6.7(dd)	6.8(s),6.9(s), 7.98(d),8.1(d), 8.8(d)	2.3(s)	310,245	134
116a	3.92(s)	5.92-6.41(dd)	7.0-7.2(m)	-	245	70
116b	3.9(s)	5.88-6.5(dd)	-	-	216.5	180
116c	4.24(s)	6.26(m),7.26(m)	7.52(s),7.7(s), 5.2(d),8.36(m), 8.93(d)	-	329,268,	130
117a	2.92(s)	5.92-6.4(dd)	7.0-7.2(m)	-	243.8	100
117b	2.8(s)	5.88-6.5(dd)	-	-	#	#
117c	2.33(s)	6.1-6.6(dd)	6.76(s),6.9(s), 7.93(d),8.1(s), 8.3(d)	-	313,241 249	124
118a	5.0(s)	6.3-6.52(dd)	7.1-7.3(m)	1.95(s)	307,240	oil
118b	4.98(s)	6.65-7.0(dd)	6.65-7.0(dd)	2.2(s)	#	#
118c	5.14(s)	6.40-7.58(m)	6.40-7.58(m)	2.28, 2.32	222	106
120a	4.1(s)	6.85-7.3(m)	6.85-7.3(m)	-	241.8	80
120b	4.1(s)	6.45-6.9(dd)	6.45-6.9(dd)	-	217.5	135
120c	4.4(c)	6.8-7.26(m)	7.5(s),7.6(s) 8.2(d),8.35(d) 8.96(d)	-	332,269,	119
121a	3.14(s)	6.56-7.08(m)	6.56-7.08(m)	-	242	98
121b	2.9(s)	6.38-6.6(dd)	6.38-6.6(dd)	-	#	#
121c	2.8(s)	6.56-7.1(m)	7.4(s),7.5(m)	-	324	120
122a	5.1(s)	6.76-7.4(m)	6.76-7.4(m)	2.0(s)	244	vis.oil
122b	4.99(s)	6.86-7.1(m)	6.86-7.1(m)	1.99(s)	#	#
122c	5.1(s)	6.9-7.0(m)	6.9-7.0(m)	2.0(s)	-	-

124a	4.0(s)	6.85-7.3(m)	6.85-7.3(m)	-	288,248	84
124b	4.15(s)	6.76-7.0(dd)	6.76-7.0(dd)	-	299,218	140
124c	4.1(s)	6.86-7.2(m)	7.38(s),7.5(s), 8.1(d),8.26(d), 8.88(d)	-	333,269, 230	124
125a	2.3(s)	6.7-7.7(dd)	6.7-7.7(dd)	6.99(s)	352,247	102
125b	3.0(s)	6.74-7.1(dd)	6.74-7.1(dd)	6.99(s)	#	#
125c	2.9(s)	6.6-7.0(m)	7.38(s),7.6(s), 8.0(d),8.2(d), 8.86(d)	-	325,235	128
126a	5.0(s)	6.8-7.2(m)	6.8-7.2(m)	1.98(s)	244	oil
126b	5.1(s)	6.86-7.1(m)	6.86-7.1(m)	1.99(s)	#	#
126c	5.1(s)	6.9-7.0(m)	6.9-7.0(m)	2.0(s)	-	-

not pure

Table 2.11 : Characteristics of ring substituted Organometallic Products [(119a-c), (123a-c), (127a-c)]

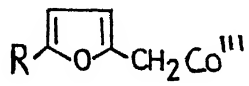
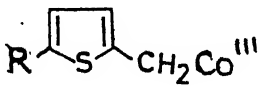
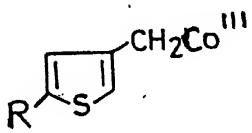
Organic Products	^{1}H NMR (Chemical shift, δ) dmgH	CH_2	Hetero-aromatic	Aromatic	UV-VIS λ_{max} (nm) (CH_3OH)
119a	2.06(s)	2.6(s)	6.02-6.4(dd)	7.1,7.2, 7.6,8.4(m)	379,240, 208
119b	2.0(s)	2.5(s)	5.96-6.4(dd)	7.2,7.5, 8.35(m)	382,217
119c	2.06(s)	2.5(s)	5.95-6.5(dd)	7.2,7.6,8.4(m), 7.66(s),7.4(s), 8.2(d),8.9(d), 9.0(d)	299,239, 207
123a	1.96(s)	2.75(s)	6.5-6.8(dd)	7.04-7.1(m), 7.2,7.4,8.35(m)	380,286, 243,208
123b	1.9(s)	2.8(s)	6.6-6.9(dd)	7.2,7.6,8.4(m)	385,290, 219
123c	2.18(s)	3.0(s)	6.8-7.08(dd)	7.34,7.8, 8.52(m),7.6(s), 7.4(s),8.28(d), 8.35(d),9.1(d)	308,241 206
127a	1.96(s)	2.76(s)	6.7-6.8(dd)	7.2(m),7.2,7.5, 8.4(m)	367,244, 209
127b	2.01(s)	2.95(s)	6.65-6.85(dd)	7.2,7.5,8.5(m)	380,237, 218
127c	2.01(s)	2.56(s)	6.7-7.0(m)	7.6(s),7.4(s), 7.7(m),8.1(d), 8.25(d),9.1(d)	306,242, 206

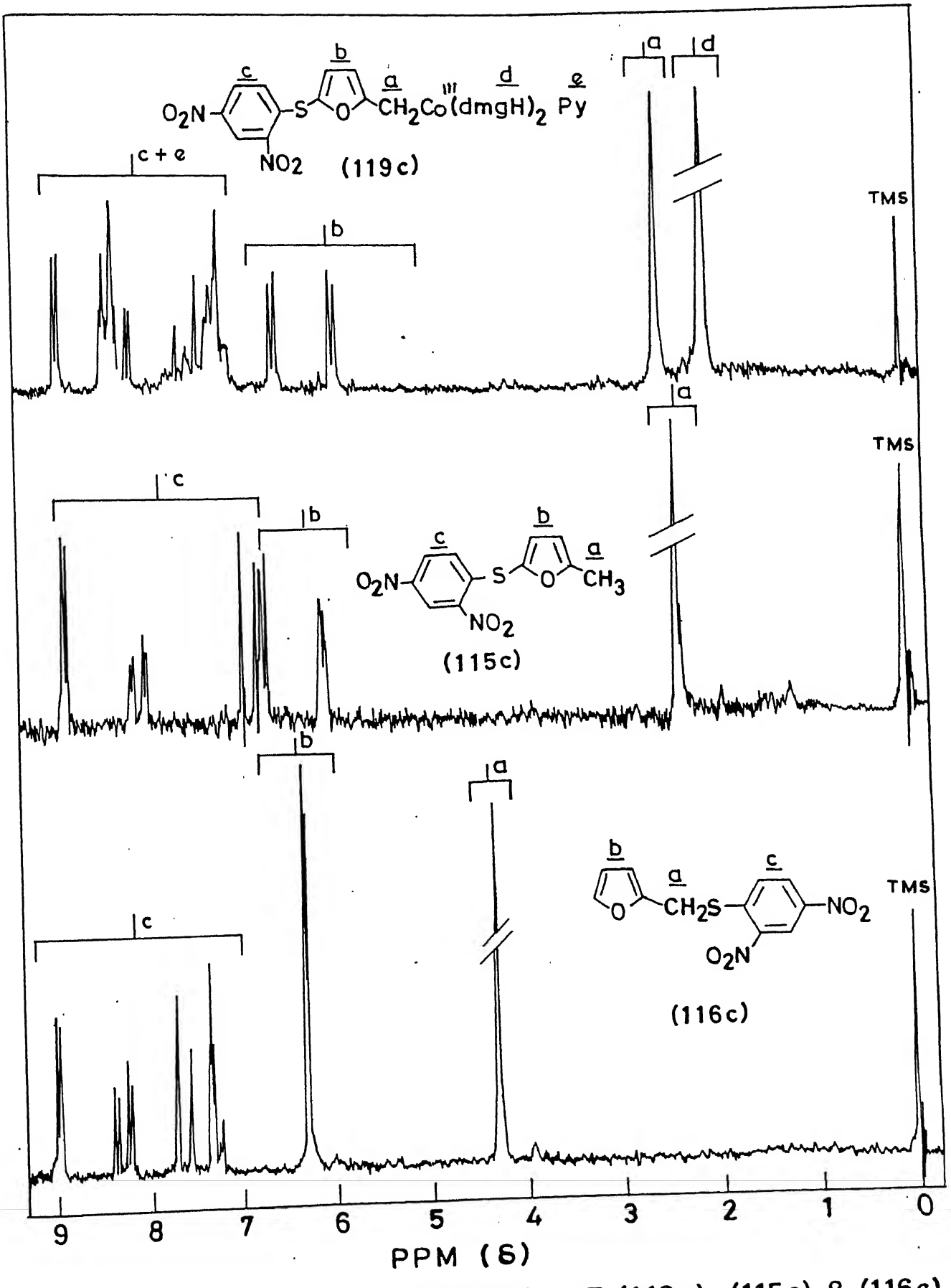
Table 2.12 : Mass spectra of organic products from the reaction of heteroaromatic methyl cobaloximes (53-55) with arene sulphenyl chloride (A, B and C)

Organic Compound No.	Mass (m/e)*
115a	190 (42.8%), 109 (100%), 218 (74%)
115b	366 (82.5%), 298 (59%), 114 (100%)
115c	280 (3.9%), 183 (24%), 152 (25%), 113 (24%)
116a	298 (3.9%), 189 (100%), 109 (95.5%)
116b	643 (6.3%), 362 (100%), 281 (12.9%), 246 (25.7)
117a	378 (23.2%), 189 (100%), 109 (97.5%)
117b	279 (74.8%), 183 (20.2%), 125 (45.1%)
118a	304 (10.9%), 218 (38.1%), 204 (89.0%), 189 (43.4%), 109 (100%)
120a	314 (6.2%), 205 (93.1%), 171 (57.2%)
120b	659 (2.4%), 378 (30.4%), 342 (100%), 246 (80.1%), 177 (88%)
121a	410 (89.1%), 301 (10.7%), 205 (100%)
121c	296 (17.0%), 183 (12%), 109 (27.9%)
122a	320 (50.6%), 220 (76.6%), 205 (100%)
124a	314 (10.1%), 205 (100%), 109 (16.8%), 128 (10.5%)
124b	378 (47.3%), 342 (100%), 246 (79.1%), 177 (99.6%)
125a	302 (62.0%), 205 (100%)
125c	296 (17.9%), 201 (22.1%), 183 (13.1%), 109 (21.2%)
126a	320 (40.5%), 220 (56.6%), 205 (100%)

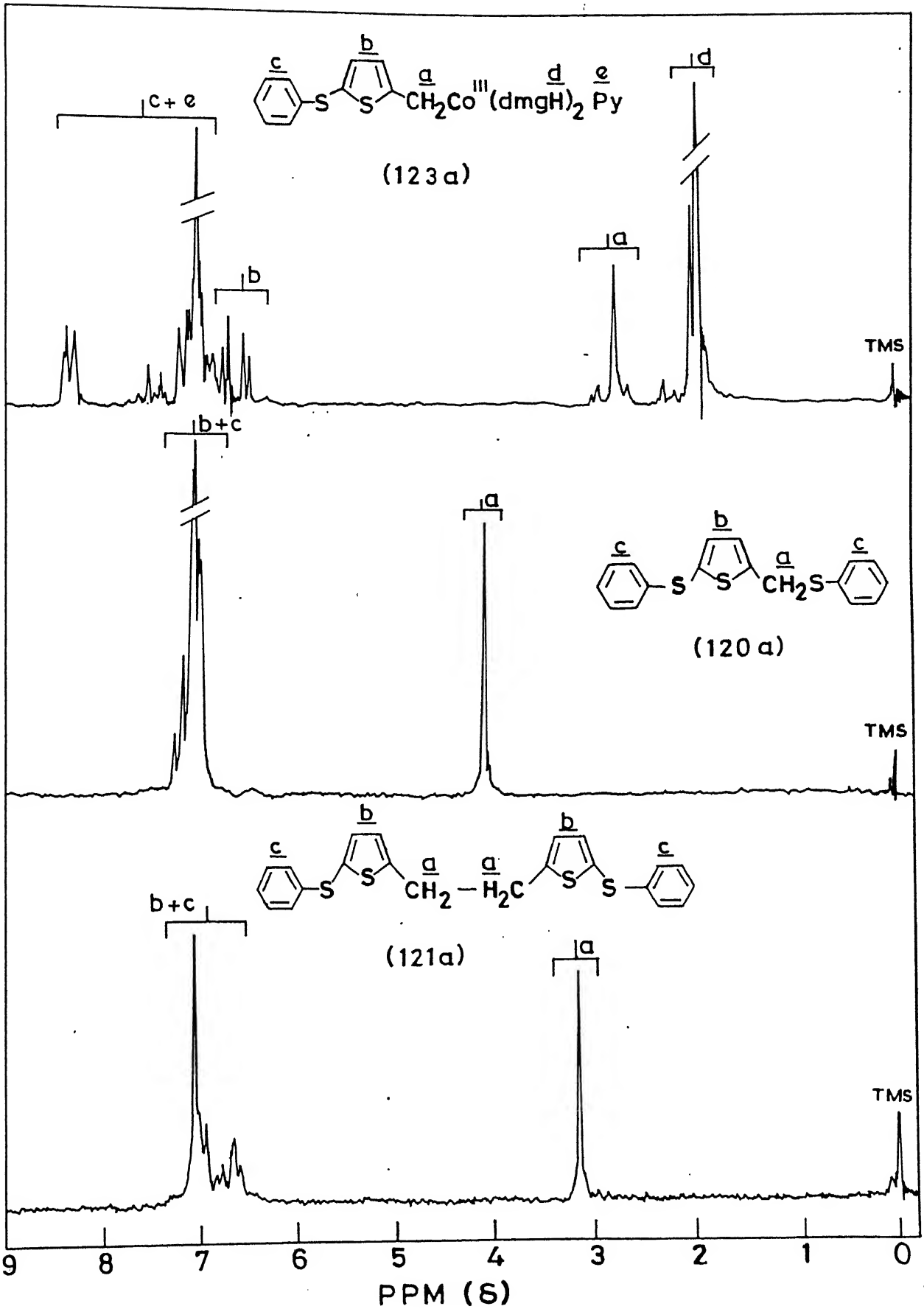
* see discussion for the fragmentation pattern

Table 2.13 : Cyclic Voltametric parameters [oxidation potential] for Organocobaloximes

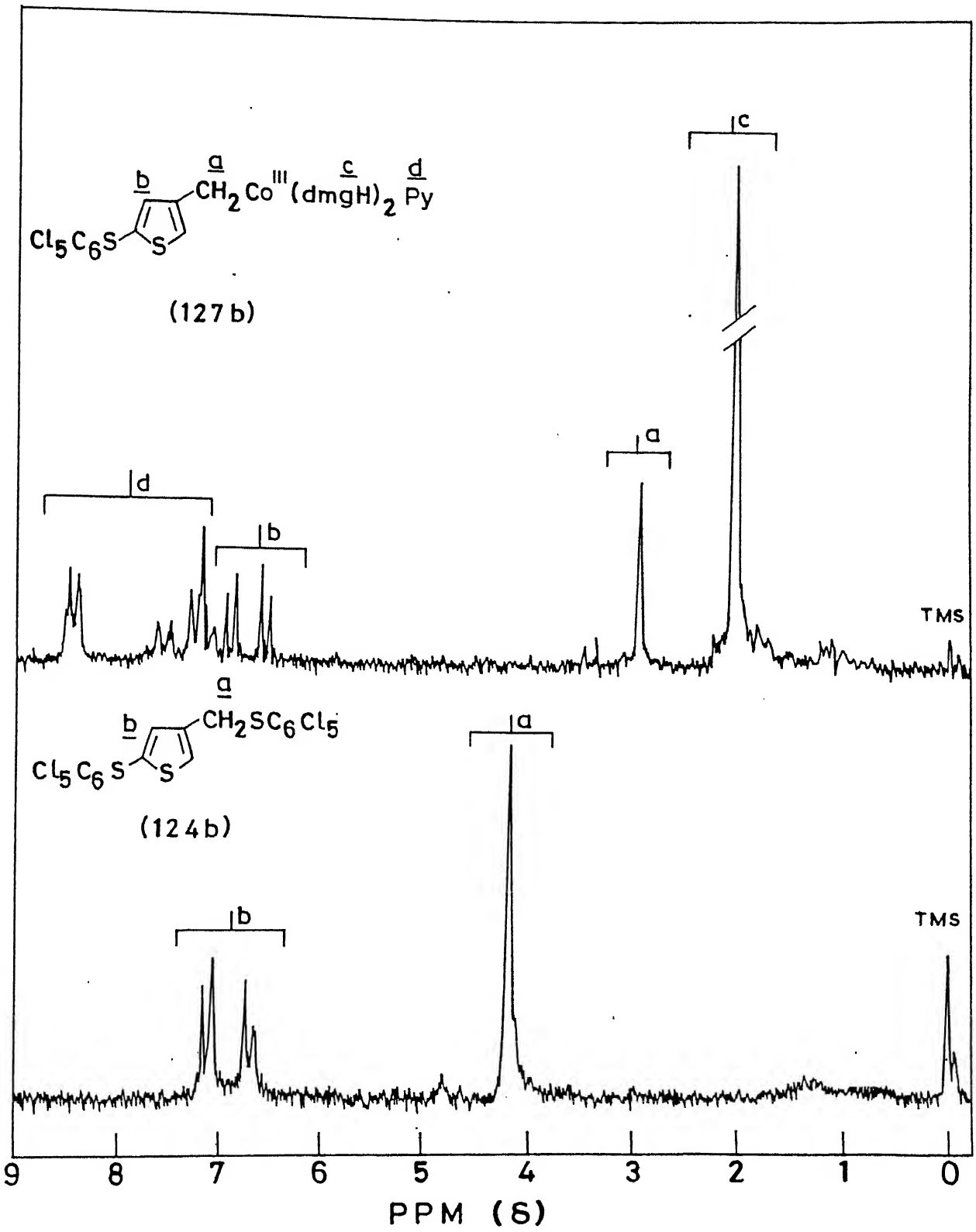
Compound No.	Organocobaloxime	R =	CV Values $E_{1/2}$, V vs. SCE
(53)		H	0.980
(119a)		SPh	0.825
(119b)		SC_6Cl_5	0.834
(119c)		$SC_6H_3(NO_2)_2$	0.9145
(54)		H	0.950
(123a)		SPh	0.899
(123b)		SC_6Cl_5	0.846
(123c)		$SC_6H_3(NO_2)_2$	1.071
(55)		H	0.923
(127a)		SPh	0.8841
(127b)		SC_6Cl_5	0.958
(127c)		$SC_6H_3(NO_2)_2$	1.011



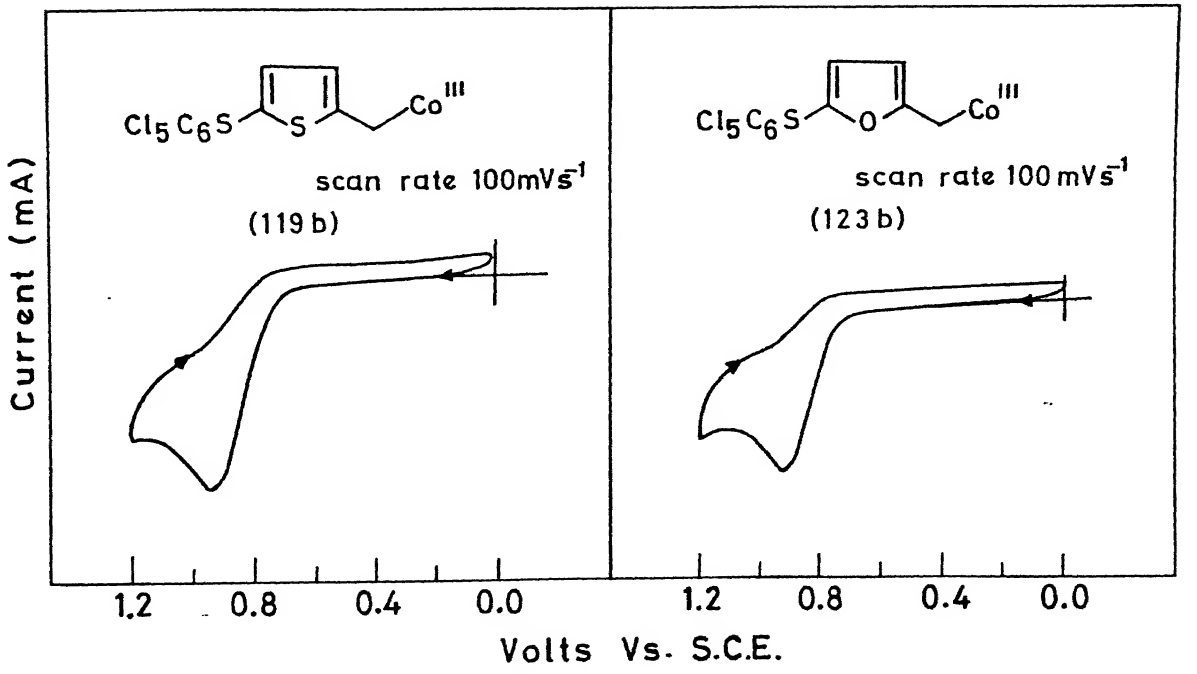
^1H NMR SPECTRA (60MHz) OF (119c), (115c) & (116c).



^1H NMR SPECTRA (60MHz) OF (123a),(120a) & (121a).

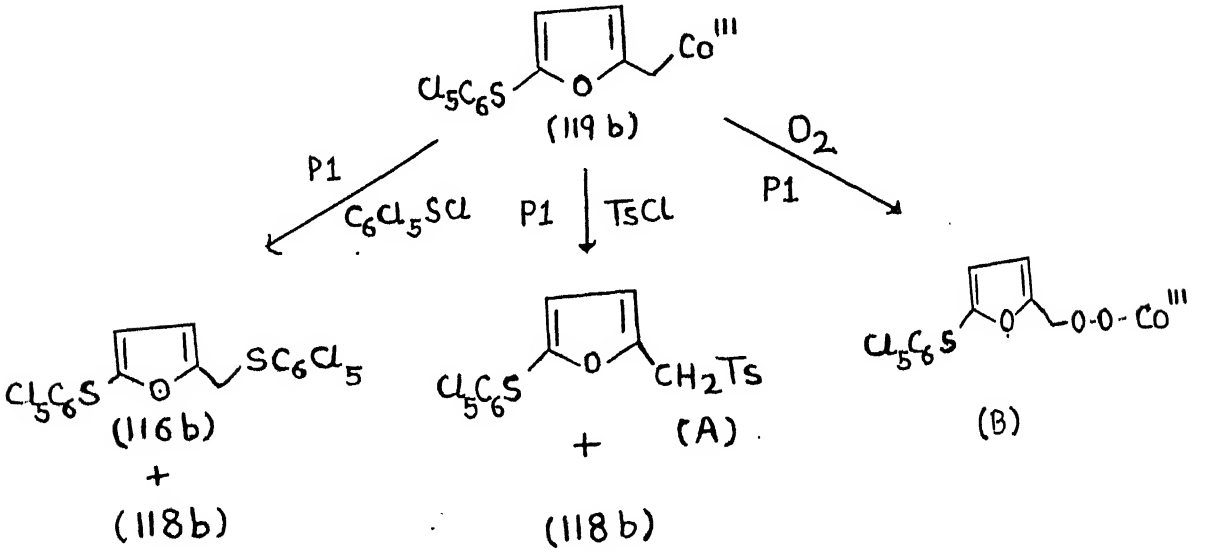


? SPECTRA (60 MHz) OF (127b) & (124b).



CYCLIC VOLTAMMOGRAM OF (119b) & (123b)

A few independent experiments on the 5-substituted furfuryl cobaloxime (119b) obtained from the reaction of (53) with (B) give the following information. The reaction of (119b) with B is slow (∝ 6 hrs) under P1 conditions and forms (116b) and (118b) and with tosyl chloride the corresponding sulphone (A) [^{1}H NMR : 4.16(s), 2.36(s), 6.33-6.5(m), 7.06-7.6(m)] and the furfuryl ether products are isolated. Furthermore, (119b) undergoes a facile oxygen insertion reaction to form the corresponding inserted product (B) [^{1}H NMR : 2.3(s), 4.26(s), 6.3- 6.7(dd), 7.2, 7.56, 8.24 (pyridine, m)] (See Scheme 2.4).



Scheme 2.4

3-Methylallyl cobaloxime (44) reacts with (B) under P1 conditions and within 25 min gives the corresponding allylsulphide (132) in 68% yield. The same reaction is faster under P2 and affords 88% yield, however, the thermal reaction is slow and gives lower yield. The similar observations are made in the reaction of other allyl cobaloximes (43-46) with (A) or (B). The reaction with (C), however, requires much higher temperature and gives much lower yield of the corresponding sulphides and a side product, O-allyl derivative of dimethylglyoxime is accompanied in each reaction. The reaction with (C) under P1 conditions is, however, not clean and forms a mixture of organic products, many of which could not be characterised.

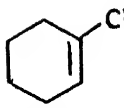
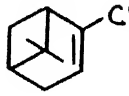
The reaction of cyclohexenyl methyl cobaloxime (47) with (A), (B) or (C) affords a complicated mixture of products which are difficult to characterise.

α-Pinenyl cobaloxime (48) is very reactive under P1 conditions and the reaction is complete within 5-10 minutes. The organic sulphides (140 and 141) obtained after the reaction of (48) with (A) and (B) respectively rearrange to the ring opened products (140' and 141') during the purification process on the silica gel column. The reaction product (142) however is very stable and no rearrangement of any kind is observed. The characteristics of the organic products are given in tables 2.14 and 2.15.

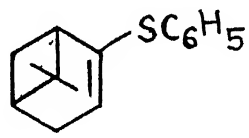
$$RCo^{III} + ArSCl \xrightarrow{h\nu/\Delta} RSAr + ClCo^{III}$$
(43-48) A,B,C (114-128) (24)

Table 2.14 Organic products from the reaction of ArSCl (A,B and C) with allyl cobaloximes (43-48)

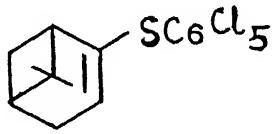
RCo^{III}	Organic Precursor	Reaction condition Time (min)	Organic Product (No.)	Yield (%)
$CH_2=CH-CH_2-$ (43)	A	P1/10	$PhSCH_2CH=CH_2$ (128)	68
	B	P1/20	$(C_6Cl_5S)CH_2CH=CH_2$ (129)	68
		P2/10	$(C_6Cl_5S)CH_2CH=CH_2$ (129)	79
	*C	T1/90	$(NO_2)_2C_6H_3SCH_2CH=CH_2$ (130)	37
$MeCH=CH-CH_2-$ (44)	A	P1/10	$MeCH(SPh)CH=CH_2$ (131)	72
	B	P1/25	$MeCH(SC_6Cl_5)CH=CH_2$ (132)	68
		P2/10	$MeCH(SC_6Cl_5)CH=CH_2$ (132)	88
		T2/45	$MeCH(SC_6Cl_5)CH=CH_2$ (132)	69
		RT/dark	$MeCH(SC_6Cl_5)CH=CH_2$ (132)	49
	*C	T1/90	$MeCH[(NO_2)_2C_6H_3S]CH=CH_2$ (133)	39
$(Me)_2C=CH-CH_2-$(45)	A	P1/10	$Me_2C(SPh)CH=CH_2$ (134)	82
	B	P1/35	$Me_2C(Cl_5C_6S)CH=CH_2$ (135)	81
		P2/10	$Me_2C(Cl_5C_6S)CH=CH_2$ (135) + $Me_2C=CHCH_2SC_6Cl_5$ (135') (9:1)	84
		T2/65	$Me_2C(Cl_5C_6S)CH=CH_2$ (135)	78
		RT/dark	$Me_2C(Cl_5C_6S)CH=CH_2$ (135)	46
	*C	T1/180	$Me_2[(NO_2)_2C_6H_3S]CH=CH_2$ (136)	38

$PhCH=CH-CH_2$-(46)	A	P1/10	$PhCH(SPh)CH=CH_2$ (137)	78
	B	P1/15	$PhCH(Cl_5C_6S)CH=CH_2$ (138)	80
		P2/10	$PhCH(Cl_5C_6S)CH=CH_2$ (138)	87
		T2/40	$PhCH(Cl_5C_6S)CH=CH_2$ (138)	80
		RT/dark/180	$PhCH(Cl_5C_6S)CH=CH_2$ (138)	50
	*C	T1/240	$PhCH[(NO_2)_2C_6H_3S]CH=CH_2$ (139)	32
 (47)	A,B & C	P1 ⟶	Complicated reaction mixture was obtained	
 (48)	A	P1/10	[(140) and (140')	48
	B	P1/10	(141) (141')	50
	C	P1/15	(142)	54

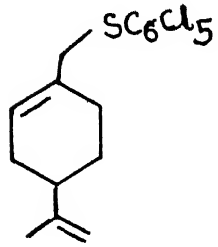
* Ref 239 g T1 = ambient temp (AcOH) . T2 = refluxing temp



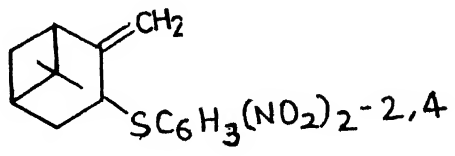
(140)



(141)



(141')



(142)

Structures of (140 - 142)

Table 2.15 : Characteristics of allyl aryl sulphides (128-142)

Product No.	M.P. (°C)	^{1}H NMR Chemical shift δ (ppm), (multiplicity), [J=Hz] H(1)	H(2)	H(3)	Aromatic	others
(128)	Liq.	3.4(d)[6]	5.4-5.98(q)	4.78-5.12(m)	7.0-7.2(m)	-
(131)	Liq.	3.5(m)	5.3-5.90(q)	4.51-4.9(bm)	7.0-7.2(m)	1.3(d)[8]
(134)	Liq.	-	5.6-6.02(q)	4.48-4.9(bm)	7.0-7.2(m)	1.3(s)
(134')	Liq	3.5(d)	5.34(m)			1.57,1.70(br)
(137)	Liq.	5.86-6.4 (bm)	4.2-5.08(m)	4.2-5.08 (m)	7.2-7.3(m)	
↘(140)						
↘(140')						
(129)	65	3.5(d)[7]	5.4-5.97(q)	4.76-5.01(m)	-	-
(132)	69	3.85(m)	5.3-5.97(q)	4.51-4.88(m)	-	1.4(d)[8]
(135)	54	-	5.67-6.2(q)	4.52-4.94(m)	-	1.47(s)
(135')	54	3.48(d)	5.2(t)	-	-	1.58(d)
(138)	85	5.94-6.4 (bm)	4.18-5.16(m)	4.18-5.16(m)	7.3-7.4(m)	-
↘(141)						
*(130)	71	3.85(d)	5.9(m)	5.48,5.45	-	
*(133)	73	4.08	-	5.16,5.30	-	1.56(d)
*(136)	-	-	6.17	5.32	-	1.6(d)
*(139)	76	5.24	6.15	5.4,5.37	-	-
↘(142)						

↘ The ^{1}H NMR values do not follow the tabulated pattern, hence are given separately as follows:

(140): 0.8(s), 1.26(s) [$>CMe_2$], 1.8-2.3(bm) [cycloalkyl], 3.4(s) [$>CH_2$], 5.4(b) [=CH], 7-7.2(m) [Ar]

(140'):1.6(s) [CH_3], 1.8-2.3(bm) [cycloalkyl], 3.36(s) [CH_2], 4.56(s) [$=CH_2$], 5.4(bs) [=CH]

(141): 1.6(s) [CH_3], 1.78-2.3(bm) [cycloalkyl], 3.36(s) [CH_2], 4.5(s) [$=CH_2$], 5.17(bs) [=CH]

(142): 0.7(s), 1.26(s) [$>CMe_2$], 1.8-2.3(bm) [cycloalkyl], 4.8-4.93(dd) [$=CH_2$], 4.3(t) [allylic H], 7.4(s), 7.66(s), 8.06(d), 8.2(d) [Ar]

* Ref. 239g

The following information is obtained from the independent reactions.

i) A slow addition of (A) or (B) (≥ 90 min.) to (48) forms a mixture of (140+140') or (141+141').

ii) No allyl chloride or allyl derivatives of dimethylglyoxime is formed in any of the reactions of allyl cobaloximes with either (A) or (B). However, the reaction with (C) forms allyl derivatives of dimethylglyoxime in each reaction.

iii) A small amount of diaryl disulphide is formed in each reaction, however its further reaction with allyl cobaloxime is very slow under the reaction conditions, for example the reaction of diphenyl disulphide with (44) under P1 condition remains incomplete even after 10 hr.

iv) The reaction of (45) with (B) under P2 conditions forms (135) and (135') in the ratio 9:1. Since the isomerisation of the kind (135) to (135') is known to occur in the presence of $Ar\dot{S}$ radicals[13], a few more observations are made from independent experiments as mentioned below.

a) γ-product once formed is quite stable and does not isomerise to the α-product, for example a pure sample of (135) is stable upto ten days when kept at room temperature under diffused light and no isomerisation to (135') is observed.

b) Though the reaction of (44) with (A) under P1 is complete within 10 min., yet even if the reaction mixture is kept under these conditions for 4 hr., γ-product (131) is the only product

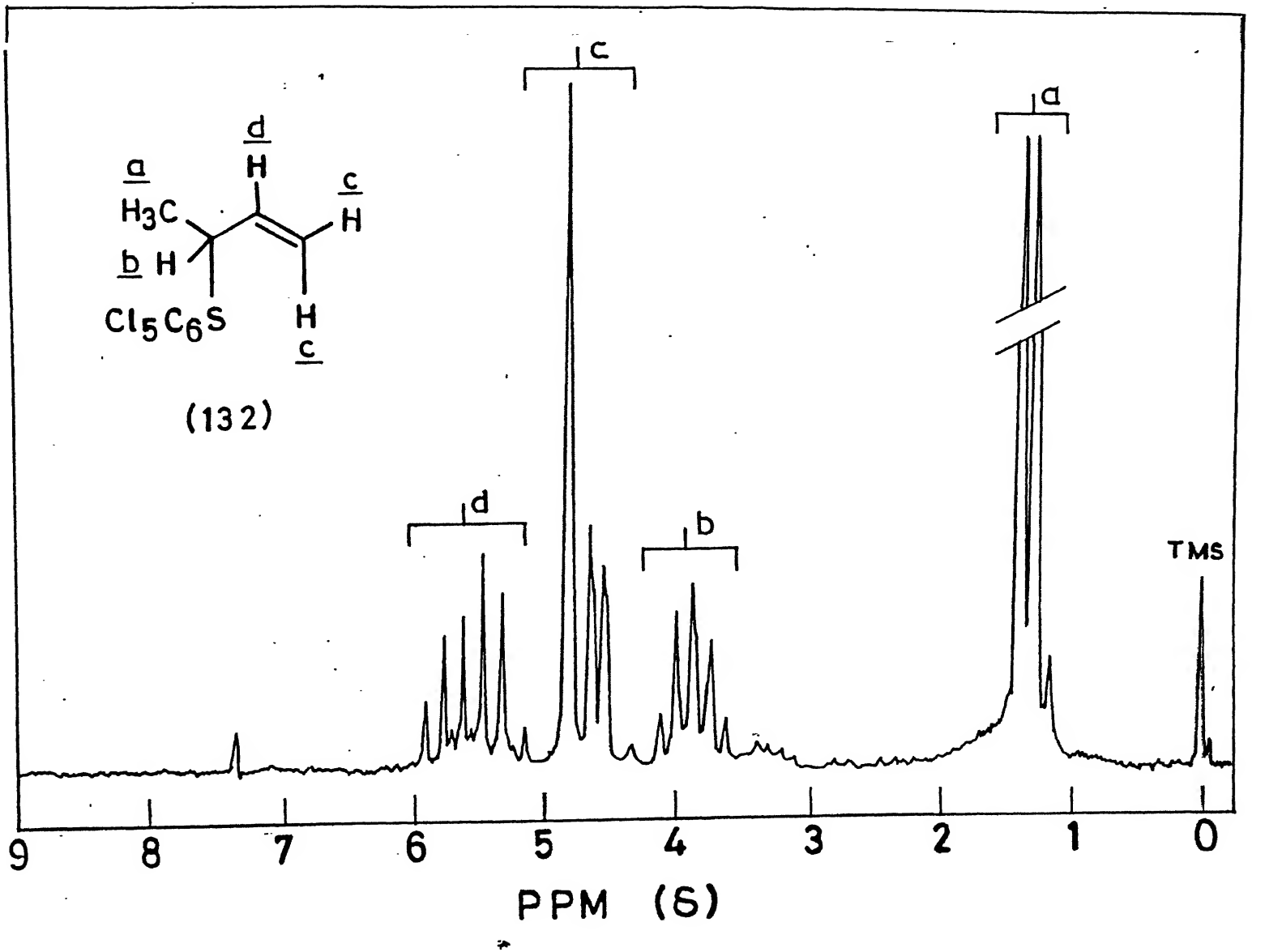
isolated. This indicates that once (131) is formed, it does not isomerise to the α-product even though the reaction mixture has excess of PhSCl and Co(II) in solution.

c) A reaction mixture (obtained from the ether work up of the reaction of (45) with (B) under P1 condition) containing (135) and a trace amount of the dimer $(C_6Cl_5S)_2$ was kept at room temperature under diffused light. The subsequent ^1H nmr studies showed that the amount of (135') started increasing after 10 days and became predominant after 30 days. However no further change was observed after this time (Fig. 1). A similar observation is made for a mixture containing (135) and (135') in the ratio 8:2 and 9:2 when kept over a period of one month.

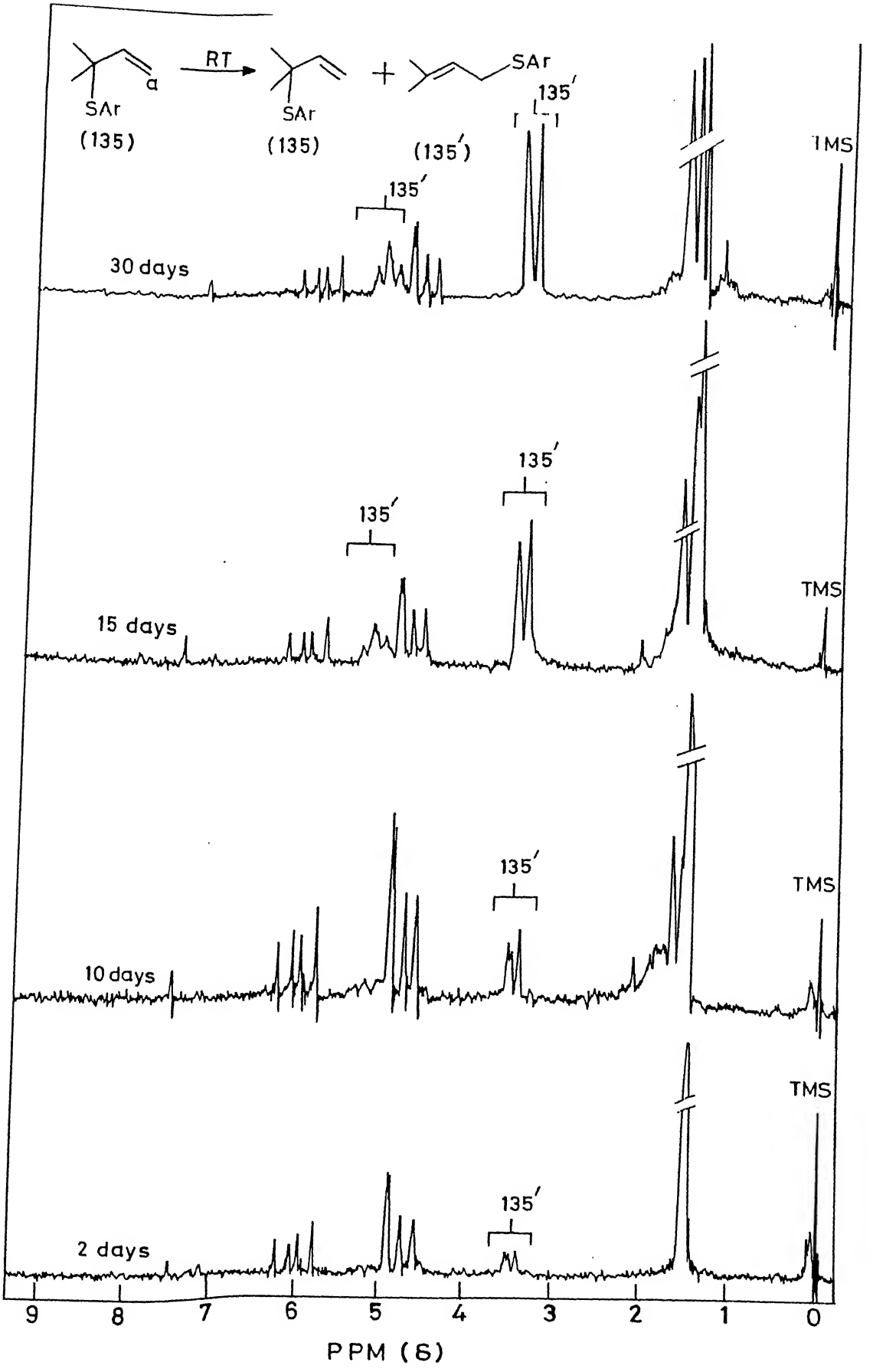
d) A reaction mixture (from (44) with (A) in $CHCl_3$) is kept under P1 conditions for 2 h., and then at 35°C overnight under diffused light, followed by heating at 70°C for 10 h. The ^1H nmr studies at each stage showed the formation of (131), the γ-product only.

The reactions of allenyl (49-50) and propargyl (51) cobaloximes with (A) and (B) are also studied. The reactions are, in general, very complicated and form a number of products, both organic and inorganic. Most of these could not be characterized.

The reaction of but-3-enyl cobaloxime (52) with (B) under P1 condition is very fast and is complete within 5 minutes and forms exclusively an organometallic product. We have not been able to arrive at the final structure of the product, however, its ^1H NMR values are 1.25-1.7(m), 2.1(bs), 3.02-3.2(m), 3.5(bs), 7.26, 7.56, 8.5 (pyridine).



^1H NMR SPECTRA (60 MHz) OF (132).



^1H NMR SPECTRA (60MHz) OF (135) & (135′). [Fig. 1]

2.4.2 Discussion

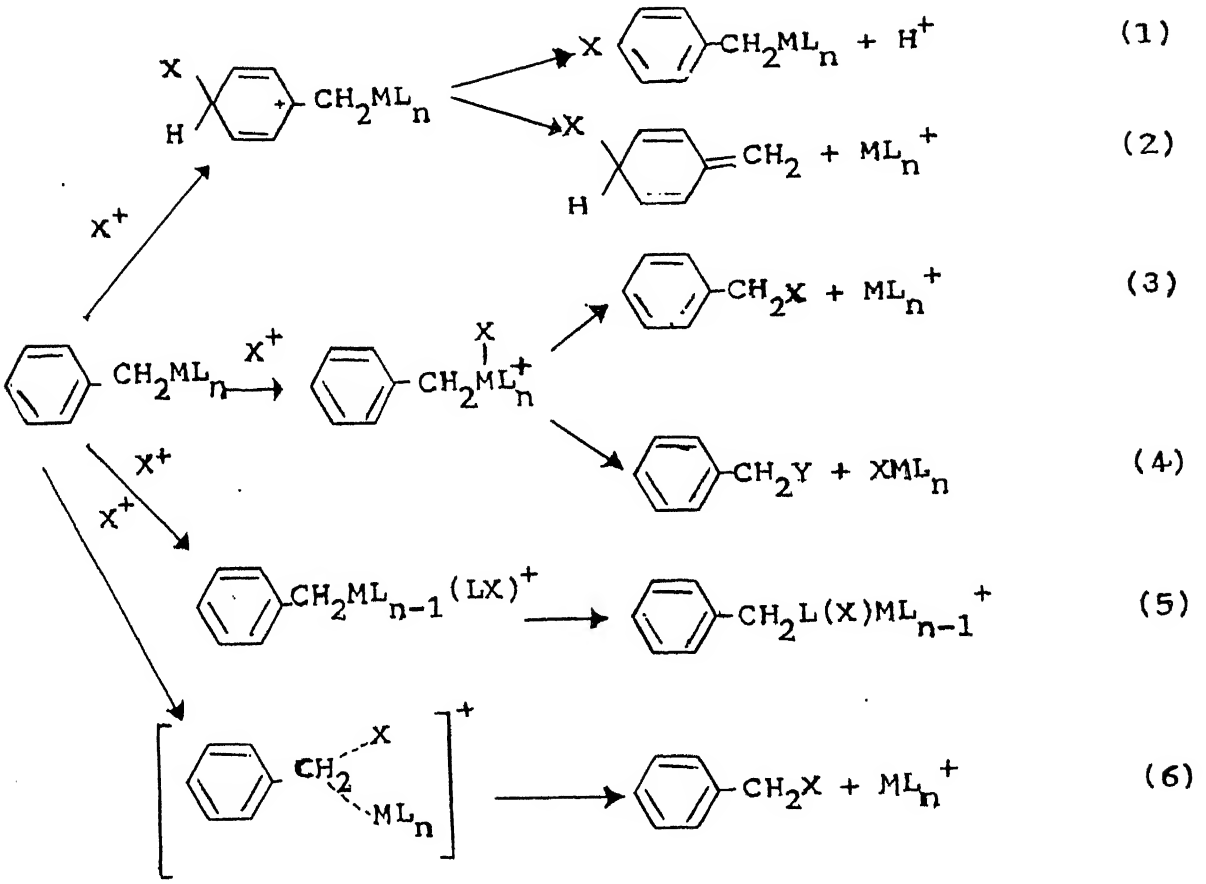
The Co-C bond in organocobaloximes is weak and its cleavage may be induced in many ways including electrophilic, nucleophilic and free radical attack at the R group, reduction or oxidation of $R\text{-}Co^{III}$, modification within the R group, charge transfer interaction of the macrocycle with additional reagents, axial ligand exchange, light or heat and steric interaction between macrocycle and the R group. The actual cleavage depends upon the nature of the R group and is often caused by combined parameters[295a].

A good deal of work has been done on the chemistry of arene sulphenyl halides, especially the chloride[295(b-d)]. Although the addition of sulphenyl halide to simple alkenes has long been known, the fundamental work on this reaction was done by Kharasch[295c] and his coworkers. Since the electrophilic addition of sulphenyl halide appears to be one of the most efficient ways to transform alkenes into synthetically useful products, it has been extensively studied and reviewed[296]. The detailed studies reveal that depending on the nature of the reagent and the experimental conditions the mechanism of this reaction can either be electrophilic or free radical in nature.

ArSCl if it reacts with organocobaloximes in a free radical manner, it may do so in a number of ways e.g. i) free radical addition at the double bond (in case of allyl and allenylcobaloximes) followed by Co-C bond cleavage, ii) Co-C bond homolysis and subsequent reactions of the generated $\dot{R}$ and iii) S_H2 or S_H2' reactions at the carbon centre displacing

cobaloxime(II)[2391].

However, if ArSCl acts as an electrophile, then in principle, it may attack at the organometal complex at a number of sites[297a] (Scheme 2.5).



Scheme 2.5

a) attack may take place at the aromatic ring (in case of benzyl and heteroaromatic methyl cobaloximes) leading to substitution[297b] (eq. 1) and/or to metal-carbon bond cleavage (eq. 2)[297c], b) attack may take place at the metal centre[297d] leading to a variety of products including those from reductive elimination (eq. 3) and from the nucleophilic displacement of the α carbon (eq. 4), attack may take place at the ligand L leading to a variety of products including those from insertion process[297e] (ligand migration, eq. 5) and attack may also occur at the α carbon (on the C-M bond orbital eq. 6)[245]. Reactions of all six type are known and the path followed is certainly a function of the particular electrophile, its interaction with the HOMO of the complex, and the nature of the reaction medium. In all cases a certain degree of electron transfer occurs[224,297a].

i) Alkyl Cobaloximes

The experimental observations point to the free radical nature of these reactions. The alkylsulphides may be formed by a direct displacement of cobaloxime(II) by attack of the $Ar\dot{S}$ radical on the α carbon of the alkyl group. A trace amount of cobaloxime(II) impurity present in organocobaloximes is sufficient to generate $Ar\dot{S}$ radical by the abstraction of Cl from the ArSCl. We do not prefer the alternative route where $\dot{R}$, formed by the unimolecular homolysis of $R\text{-}Co^{III}$, attacks the sulphur centre of ArSCl to form ArSR. As the alkyl radicals are known to abstract halogen from ArSCl and have the tendency to dimerisation[296b], a complete absence of both these products i.e. RCl and R-R supports the above viewpoint.

ii) Benzyl Cobaloximes

The similar argument may be extended to the reactions of benzyl cobaloximes with A and B. The close similarity between the thermal and photochemical reaction (see table 2.4, the reaction of (34) with B under P1, P2 and T) supports that the same radical processes are involved in both sets of conditions. The benzyl sulphide may be formed by a direct displacement of cobaloxime(II) by attack of the $Ar\dot{S}$ radical on the α carbon of the benzyl group.

However, in the reaction with (C) the formation of bibenzyl is indicative of the presence, of benzyl radical as intermediate, which are known to dimerise fast and the formation of benzyl ethers of dimethylglyoxime points to the intermediate formation of organocobalt(IV) species in solution[239i]. Such similar ether products are known to form as side products in many electrophilic and free radicals reactions of organocobaloximes[52b,240,298]. The identical products are also formed when the benzylcobaloximes are chemically oxidised by Mn(III) acetate[299a]. The stability and existence of RCo^{IV} has been confirmed by Halpern et.al. in their oxidation study of benzyl (aquo) cobaloxime with $IrCl_6^{2-}$ [212,218]. We do not wish to discuss their formation in detail, however, since these are observed in the thermal but not in the photochemical reaction with ArSCl, it is clear that they are not formed as a result of the attack of the $Ar\dot{S}$ on any atom of the organocobaloxime substrate under the condition of thermal reactions, the competing heterolytic reactions involving modification of organocobaloxime, either by removal of axial pyridine ligand or by direct reaction with the equatorial ligands, probably diminish the dominance of the direct S_H2 reaction (eq.

85) both through the change in nature of the substrate and the removal of ArSCl from the system.

$$ArS^{\cdot} + PhCH_2\text{-}Co^{III}(dmgH)_2Py \longrightarrow ArSCH_2Ph + Co^{II}(dmgH)_2Py \quad (85)$$

Interestingly, 3-methoxy benzyl cobaloxime undergoes a facile ring substitution with (A) under dark indicating that the ring is highly activated. This result resembles more with the heteroaromatic methyl cobaloximes (discussed later).

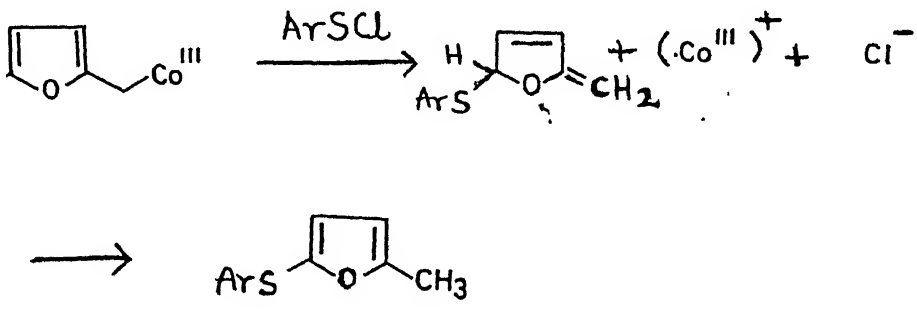
iii) Heteroaromatic methyl cobaloximes (53-55)

The reactions of heteroaromatic methyl cobaloximes (53-55) with (A), (B) and (C), in general, are complicated. A mixture of products including organic and organometallic products is formed in each reaction. The product distribution suggests that these reactions proceed by a mixture of mechanism. In general, the following useful information emerges out of the study.

a) The reaction of (53-55) with (A) and (B) under P1 condition forms four ring substituted products in each reaction. We believe that the ring substitution is the primary step followed by the Co-C bond cleavage. The dimer (117a-c, 121a-c, 125a-c) and the heteroaromatic methyl ether of dimethylglyoxime (118a-b, 122a-b, 126) are formed by the electron transfer process as explained earlier for the benzyl case and the disulphide (116a-b, 120a-b, 124a-b) may arise either by a direct S_H2 or S_E2 process at the α carbon of the ring sugstituted organometallic product (119a-b, 123a-b and 127a-b). Interestingly, the ring substituted organometallic is the only product isolated under dark. The reactivity of (C) with (53-55) however, is different from (A) and

(B), for example, the Co-C bond in the parent cobaloxime (53-55) undergoes a fast reaction to form the corresponding sulphide and the heteroaromatic methyl ether of dimethylglyoxime. The ring substitution also occurs though to a smaller extent, as evidenced by the formation of the ring substituted dimer. The TLC monitoring of the reaction clearly shows the formation of the ring substituted organocobaloxime in the initial stages of the reaction and this then vanishes away as the reaction proceeds to completion.

b) An additional product, the ring substituted 2-methyl furan is formed as a side product in the reaction of furfuryl cobaloxime (53) with (A), (B) and (C) under all conditions. This is a novel product and is rarely seen in such kind of studies. The following mechanism is proposed for its formation



A similar mechanism has been proposed by us ealier for the formation of ring halogenated toluene in the halogenation of 4-methoxy benzyl cobaloxime [299b].

c) The yield of the ring substituted organocobaloxime is the maximum with (B) in all cases.

d) The oxidation potential value of the ring substituted organocobaloximes are comparable to the parent cobaloximes and are

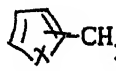
irreversible in nature.

e) A direct contrast in the reactivity of the Co-C bond in the parent cobaloximes and in the ring substituted organocobaloximes is observed, for example, in the reaction of (119b) with tosyl chloride under P1 conditions the corresponding sulphone and the 5-substituted heteroaromatic methyl ether of dimethylglyoxime are formed. However, in contrast, the same reaction with the parent cobaloxime (53) forms the sulphone exclusively. A similar observation is made in the reaction of (119b) with (B) under P1 conditions. This suggests that the substitition in the heteroaromatic ring perhaps induces the electron transfer process (Scheme 2.4).

f) The ring substituted organocobaloxime undergoes a facile oxygen insertion just like the parent cobaloxime (see Scheme 2.4).

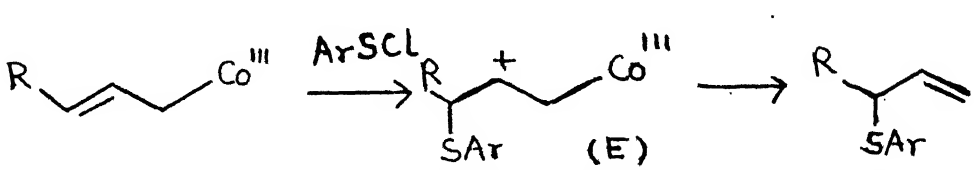
g) All efforts to introduce a second -SAr group into the heteroaromatic ring have failed. It shows that a combined substituent effect of $-CH_2Co^{III}(dmgH)_2Py$, (a conjugatively electron releasing group) and -SAr, (an electron withdrawing group) does not make the heteroaromatic ring activated enough towards this electrophile -SAr.

Mass fragmentation pattern of the organic products obtained from the reaction of heteroaromatic methyl cobaloximes (53-55) with (A), (B) and (C) is presented in Table 2.12. No simple fragmenta- tion pattern emerges for these compounds though they do reflect some important similarities in their own series, i.e., organic sulphides (116a-b, 120a-b and 124a-b), dimers (117a-c, 121a-c, 125a-c), 5-substituted methyl furan (115a-c) and organic

ethers (118a, 122a, 126a). Base peak corresponds to the mass of the fragment [M^+-ring substituted SPh or SC_6Cl_5] in all compounds except the dimers and organic ethers, however, in the dimer it corresponds to the monomer mass. Furthermore, the fragments like SPh,  -CH_2 (X=O,S), SC_6Cl_5, SC_6Cl_4, SC_6Cl_3, $SC_6H_3(NO_2)_2$, $SC_6H_3(NO)$ etc. are distinctly seen in the mass spectra of these compounds. Though no clear cut similarity in fragmentation pattern is observed in the series, (for these newly reported compounds), however, the compounds are clearly identified and the results are interesting.

iv) Allyl Cobaloximes :

From the regiospecific nature of products and the free radical nature of these reactions it seems that a direct S_H2' attack of $\dot{S}Ar$ at the γ carbon of the allyl cobaloxime is the most prominent process for reactions with (A) and (B), and we believe that the mechanism is similar to that, as proposed by us, for the same substrates with arene sulphonyl chloride[2391]. However, the electrophile attack of sulphur on the carbon centre with synchronous or subsequent loss of cobaloxime(III) is significant for reactions with (C). The reaction mechanism is thought to involve addition of the electrophile to the double bond to form the electron deficient intermediate like (E) followed by heterolytic cleavage of Co-C bond



These reactions parallel the corresponding reactions of allyl tributyl tin compounds with arene sulphenyl chloride[300].

Interestingly, in the reaction of (45) with (B), an additional product (135', 10%) is also formed. This may arise either by a direct attack of the -ṠAr radical on the α carbon of the allyl group or by a rearrangement of the less stable isomer (135) under the reaction conditions. Such rearrangements are known to occur in the literature[301] under high temperature and under acidic condition. The experimental details, however, suggest that such a rearrangement is very slow in the present studies and we believe that it may be the first example of a homolytic attack of sulphur centred radical on the α carbon of the allyl cobaloximes. Since diaryldisulphide is also formed as a side product in each reaction, its further reaction with allyl cobaloxime may also form the same allyl arylsulphides. However, this possibility is ruled out as diaryldisulphide reacts very slowly under the reaction conditions (see results).

The formation of the ring opened products in the reaction of α-pinenylmethyl cobaloxime (48) with (A) and (B) is quite interesting and needs further investigation. Such similar ring opened products are known to form in the free radical reactions of α-pinene[302]. The absence of such ring opened products in the reaction of (48) with (C) further supports that the mechanism with (A) and (B) is different from (C). This is not surprising as it is quite likely that the nitro group present in the ortho position in (C) may enhance the ionic nature of the sulphenyl sulphur[303].

CHAPTER - 3

CLEAVAGE OF COBALT CARBON BOND IN ORGANOCOBALOXIMES BY THIOCYANOGEN

3.1 AIM OF THE STUDY

Several σ bonded organotransition metal complexes are known to be susceptible to M-C bond cleavage by electrophiles[304]. Organopentaaquochromium(III) ions, by far, offer the most clean reactions[74,242,244]. The most interesting, yet less understood substrates include the organocobalt(III) complexes[42]. This is because of the seemingly endless variety of reactions they may undergo. Though studies with Hg^{+2} have led to a more rationalised picture about the mode of M-C bond cleavage[305], considerable complexities arise with halogens because of the attack of the latter at various sites of the complex and many mechanisms have been proposed for such a cleavage[297]. Thiocyanogen, as a pseudohalogen, offers analogy with halogens except for its mild reactivity and low oxidising ability*. Furthermore, this being a heteronuclear species having two reactive sites (S and N), it offers a better probe to study the mechanistic features from the point of view of the products themselves. Since the mechanism through which the Co-C bond is cleaved and the factors that promote or inhibit such cleavage are of considerable importance, the study with thiocyanogen should prove useful.

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* The reactivity of thiocyanogen falls between Br_2 and I_2 and $(SCN)_2/(SCN)_2^{\div}$ ($E^o = 0.783$)[306a].

3.2 Background

Thiocyanogen is a useful reagent for the preparation of organic thiocyanates and much work seeking analogy with halogens (for addition and substitution reactions) has been done[306a,307]. The work has supported both heterolytic as well as homolytic mechanisms depending upon the substrates, conditions and solvents etc. Under heterolytic conditions, thiocyanogen acts as an electrophile and undergoes heterolytic S-S fission

$$Nü + NCS\text{-}SCN \longrightarrow NuSCN + (SCN)^- \qquad (86)$$

The reactions of thiocyanogen are more facile with compounds having π or p electrons. Several aromatic compounds having electron releasing groups in the aromatic ring react effectively with thiocyanogen[306a,308,309] and a S_E2 mechanism is proposed for such reactions[306a]. Similarly, many heteroaromatic compounds react with thiocyanogen under very mild conditions[306a,310]. However, the reports on the reactions of thiocyanogen with metal complexes and organometallic compounds are rather few[306c,311,312]. Heterolytic reactions of thiocyanogen are usually carried out either in the dark or in diffused light. The S-S bond of thiocyanogen is readily cleaved homolytically[313] by UV or visible light. The resulting thiocyanogen radical is resonance stabilised[314].

$$(SCN)_2 \xrightarrow{h\nu} 2\dot{S}\text{-}C{\equiv}N \longleftrightarrow S{=}C{=}\dot{N}$$

Thiocyanogen radical, therefore, behaves like an acceptor radical and its reactions are restricted to systems having enhanced π electron density like benzylic, allylic, butenylic systems. Organocobaloximes, particularly allyl and but-3-enyl cobaloximes, are prone to reactions with both electrophilic[239g,263] and free

radical reagents[122,185,239(c-m),240-242] and give the rearranged allyl and cyclopropylcarbinyl sulphides and sulphones.

In most cases, especially where the reagent is not particularly electrophilic or where the electrophilic centre is different from the reactive site of the free radical, the distinction between the two mechanism may readily be established. However, when the reagent is symmetrical, of the form X_2, where reaction through electrophilic, through radical or even through nucleophilic species may lead to identical products, the mechanism is difficult to establish. Nevertheless, such reactions may still provide useful synthetic processes.

3.3 Experimental

The general experimental procedures including details of solvents, gases, chromatography, physical measurements and instruments are same as those described earlier in Chapter 2 sec. 2.2.

Starting Materials and Organocobaloximes

n-Bu(1), benzyl(2), 3,3 dimethyl allyl(3), 3-phenyl allyl(4), but-3-emyl(5) cobaloximes were synthesised by procedures as outlined in Chapter 2, p 74. 3-methyl but-3-enyl (6) and 5-methyl-hex-5-enyl (7) cobaloximes were taken from a fellow worker in the lab.

Lead thiocyanate and bromine were commercial materials and were used as such without any further purification. Thiocyanogen was prepared freshly for each experiment as described below.

A solution of bromine (10% solution, 4.3 mmol in 10 ml chloroform) was added dropwise to a stirred suspension of lead thiocyanate (4 fold excess, 5.6 g, 17.3 mmol in 20 ml chloroform). The suspension was stirred for additional 20 min after the bromine colour was discharged. The solution was used immediately after filtration.

Lead thiocyanate was prepared from potassium thiocyanate (19.4g, in 85 ml water) and lead(II) nitrate (33.1g in 150 ml water) following the procedure of Gardener and Weinberger[315].

3.4 Reaction of RCo(III) with thiocyanogen

The fresh solution of thiocyanogen (4.3 mmol in 30 ml chloroform) was added to a solution of the organocobaloxime (2.1 mmol in 20 ml chloroform) at ambient temperature under nitrogen atmosphere. The course of the reaction was monitored by TLC on silica gel. On completion, the reaction mixture was poured into excess pentane. The pentane was removed in vacuo and the crude organic product was separated on the silica gel column.

Reaction of 3-Phenylallyl cobaloxime(4) with thiocyanogen at low temperature

For this reaction the solution of the cobaloxime(4) in $CDCl_3$ was frozen and the solution of thiocyanogen in $CDCl_3$ was added directly to the NMR tube which was then allowed to warm to $-38^{\circ}C$ and kept at this temperature and the ^1H NMR spectra were recorded. The solution was then warmed to $-10^{\circ}C$ and repeated the same NMR recordings.

Table 3.1

Organic products from the reactions of RCo(III) with thiocyanogen

RCo[d]	T/°C/time(min)	Yield(%)	Organic products (ratio)[a]
1	2	3	4
(1)	ambient/60	85	(8)n-BuSCN
(2)	ambient/90	70	(9)$PhCH_2SCN$
(3)	-38/180	b	(10a)$Me_2C:CHCH_2SCN$(50) (10b)$CH_2:CHCMe_2SCN$(50)
	-10/10	b	(10a)$Me_2C:CHCH_2SCN$(50) (10c)$Me_2C:CHCH_2NCS$(50)
	0 or 25/10	74	(10a)$Me_2C:CHCH_2SCN$(22) (10c)$Me_2C:CHCH_2NCS$(68)
(4)	-38/180	b	(11a)$PhCH:CHCH_2SCN$(70) (11b)$CH_2:CHCHPhSCN$(30)
	-10/60	b	(11a)$PhCH:CHCH_2SCN$(70) (11c)$PhCH:CHCH_2NCS$(30)
	0 or 25/10	80	(11a)$PhCH:CHCH_2SCN$(30)[c] (11c)$PhCH:CHCH_2NCS$(70)
(5)	ambient/5	65	(12a)$CH_2:CHCH_2CH_2SCN$(30)[c] (12b)cyclopropylCH_2SCN(70)
(6)	ambient/10	70	(13)1-methylcyclopropylCH_2SCN
(7)	ambient/30	55	(14)$CH_2:CMe(CH_2)_4SCN$

a Yield of isolated product, b product not isolated, identified by ^1H NMR; yield (70%)

c Proportion isolated after work-up at ambient temperature.

d The cobaloximes (1-7) are numbered as n-Butyl(1), benzyl(3), 3,3 dimethylallyl(3), 3-Phenylallyl(4), but-3-enyl(5), 3 methyl but-3-enyl(6) and 5-methyl-hex-5-enyl(7). This numbering is done for convenience only. Note that some of these cobaloximes have appeared in Chapter 2 in experimental sections under different numbers.

3.5 Results :

n-Butyl and benzyl cobaloximes(1 and 2; 3 mmol each in dichloromethane) reacts with thiocyanogen (5 mmol) within 1h at room temperature to give n-butyl and benzyl thiocyanate (8 and 9 respectively) in good yield, together with NCSCo(III) as the inorganic product.

3-Phenylallylcobaloxime(4) reacts under the identical reaction conditions to give two products (11a and 11c) in 30:70 ratio. At the reaction temperature -38°C, two products (11a) and (11b) in the ratio 70:30 were observed in the ^{1}H NMR. The product (11b) with a half life of approximately 25 min. changed smoothly to (11c) when the temperature was raised to -10°C. A similar observation was made for 3,3 dimethylallyl cobaloxime(3), (see scheme 3.1)* But-3-enyl and 3-methylbut-3-enylcobaloximes (5 and 6) similarly react very fast with thiocyanogen at ambient temperature to give (12a and 12b, 30:70) and (13) respectively. 5-Methyl-hex5enylcobaloxime(7) forms (14)in 55% yield.

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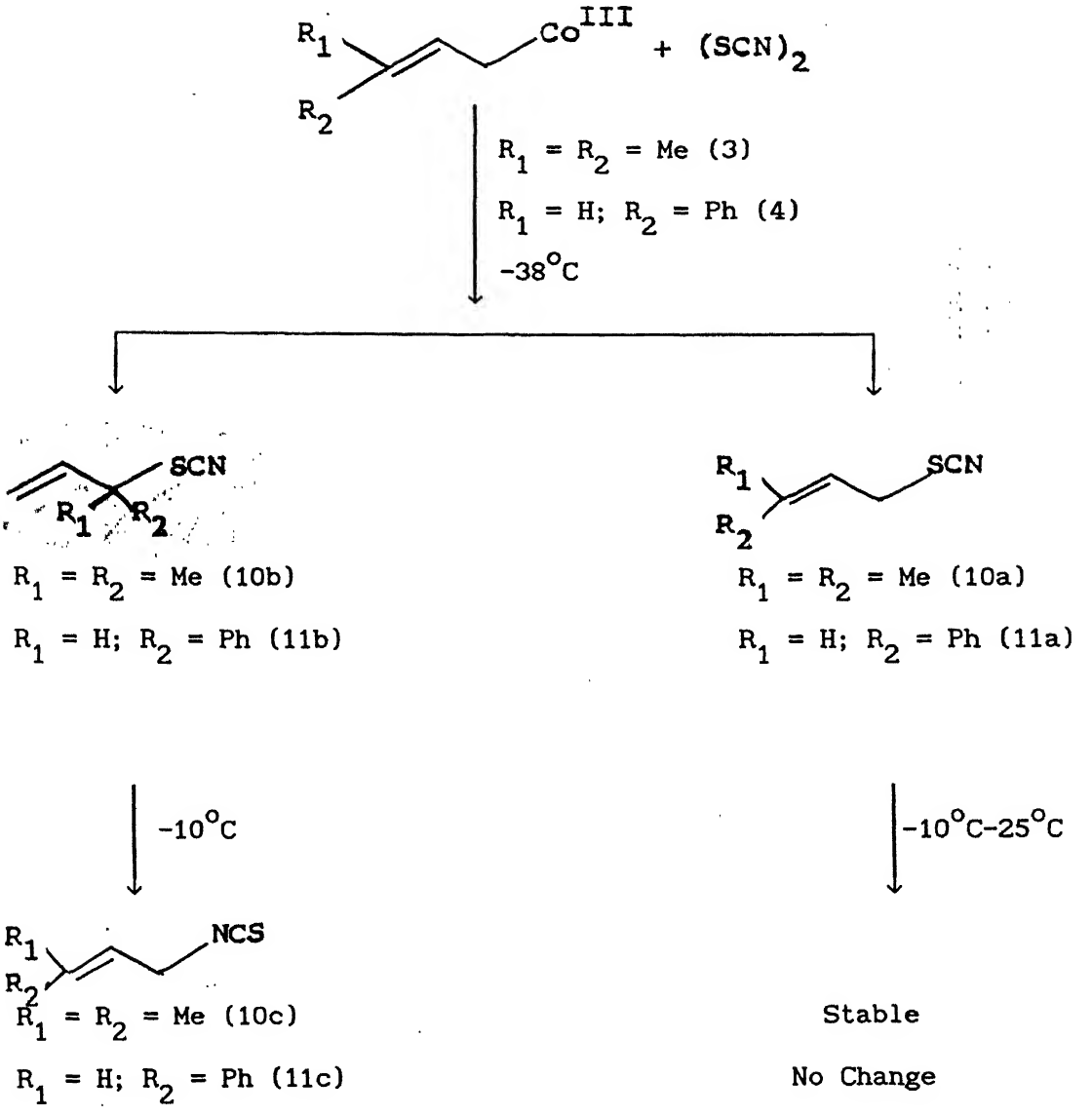
* The low temperature work was carried out at the University College London, England.


R1
R2
Co III
+ (SCN)2
R1 = R2 = Me (3)
R1 = H; R2 = Ph (4)
-38°C
SCN
R1
R2
R1 = R2 = Me (10b)
R1 = H; R2 = Ph (11b)
R1
R2
SCN
R1 = R2 = Me (10a)
R1 = H; R2 = Ph (11a)
-10°C
-10°C-25°C
R1
R2
NCS
R1 = R2 = Me (10c)
R1 = H; R2 = Ph (11c)
Stable
No Change

Scheme 3.1

^{1}H NMR of the organic products (8-14)*

[Chemical shift(δ) (ppm) (multiplicity) [J = Hz]

(8) : 0.88 (t, 3H), 1.0-2.0 (m, 4H), 2.98 (t, 2H)

(9) : 4.15 (s, 2H), 7.34 (m, 5H)

(10a) : 1.78 (s, 3H), 1.82 (s, 3H), 3.70(d, 2H), 5.4 (t, 3H)

(10b) : 1.50 (s, 6H), 5.15 (d, 1H, J = 10 Hz), 5.36 (d, 1H, J = 16.8 Hz), 5.85 (m, 1H)

(10c) : 1.70 (s, 3H), 1.77 (s, 3H), 4.12 (d, 2H), 5.37 (t, 1H)

(11a) : 3.74 (d, 2H), 6.22 (m, 1H), 6.66 (d, 1H), 7.4 (m, 5H)

(11b) : 5.06 (d, 1H), 5.38 (d, 1H, J = 10 Hz), 5.48 (d, 1H, J = 17 Hz), aromatic resonance obscured

(11c) : 4.3 (m, 2H), 6.12 (m, 1H), 6.70 (d, 1H), 7.34 (m, 5H)

(12a) : 2.58 (m, 2H), 3.60 (t, 2H), 5.15 (2d, 2H), 5.82 (m, 1H)

(12b) : 0.2-1.6 (m, 5H), 2.96 (d, 2H)

(13) : 0.59 (m, 4H), 1.25 (s, 3H), 3.03 (s, 2H)

(14) : 0.7-2.1 (m, 8H), 1.65 (s, 3H), 2.91 (t, 2H), 4.62 (s, 1H), 4.70 (s, 1H)

* ν_{SCN} : 2150-2165 cm^{-1} and ν_{NCS} = 2070-2075 cm^{-1} and all compounds give satisfactory C, H, S and N analyses

3.6 Discussion

The reactions of organocobaloximes with $(SCN)_2$ are clean and provide useful new synthesis of organic thiocyanates, especially of cyclopropylcarbinyl thiocyanate from open chain precursors and, at low temperature, of highly unstable allyl thiocyanate such as (10b) and (11b). Primary allyl thiocyanate are known to rearrange into the isomeric allyl isothiocyanates[316] but ours is the first

observations of the formation and subsequent rearrangement of the highly unstable secondary/tertiary aryl/alkylallyl thiocyanates.

The most unusual feature of these reactions is the high proportion of products of substitution at the α carbon of the organic ligand in organocobaloxime, whether alkyl, allyl or butenyl. In the previous studies alkyl cobaloximes[317] were very unreactive and with other substrates, where possible, attack at an olefinic carbon was a dominant process, both in the free radical and electrophilic displacements[122,185,239(c-m),263]. Because of the formation of polymeric thiocyanogen, as a side product, detailed mechanistic studies on these reaction could not be carried out. However, the unusual combination of very high rates of reactions of the allylcobaloximes coupled with the unusual product distribution does suggest that we are dealing with a mixture of mecanisms which include free radical processes.

The rapid formation of allyl thiocyanates indicate that thiocyanogen is particularly electrophilic towards these species with little specificity for saturated or unsaturated carbon. However, thiocyanogen is not a particularly effective nucleophile towards unsaturated carbon and the formation of primary allyl thiocyanates and of alkyl thiocyanates may also be rationalised in terms of a conventional nucleophilic attack (either S_N2 or S_N2') by thiocyanate ion[318] on intermediate organocobaloxime(IV) complex (eq. 89). The latter may be formed by oxidation of the RCo^{III} substrate with either SCN radical or $(SCN)_2$ (eq. 87 and 88); in each case giving the required nucleophilic thiocyanate ion. It is to be noted that the reduction potential of thiocyanogen (0.783 V) is slightly lower than the oxidation potential of

organocobaloximes (> 0.80 V). Therefore, it is quite unlikely that thiocyanogen is able to oxidise organocobaloximes. The absence of the organoethers of dimethylglyoxime, a characteristic decomposition product of the intermediate organocobalt(IV) as observed in reactions with benzyl cobaloximes support this view point[319]. However, since thiocyanate radicals are generated indirectly through reaction of Co^{II} with $(SCN)_2$ (eq. 90), another consequence of this primary oxidation step is likely to be the initiation of radical processes such as those shown in (eq. 91 and 92). The balance between the oxidation/nucleophilic displacement mechanism and the consequent free radical processes will thus depend upon the extent of termination in the latter. The variability of the yields of open chain and closed chain products (92a and 92b) from but-3-enyl cobaloxime supports this hypothesis. Some products may arise from organic radicals as in (eq. 93 and 94)

$$(SCN)_2 + RCo^{III}(dmgH)_2Py \rightleftharpoons (SCN)_2^{\cdot -} + (RCo(dmgH)_2Py)^+ \quad (87)$$

$$(SCN)_2^{\cdot -} \longrightarrow NCS^- + NC\dot{S} \quad (88)$$

$$NCS^- + (RCo(dmgH)_2Py)^+ \longrightarrow RSCN/RNCS + \dot{C}o(dmgH)_2Py \quad (89)$$

$$(SCN)_2 + \dot{C}o(dmgH)_2Py \longrightarrow NC\dot{S} + NCS\ Co^{III}(dmgH)_2Py \quad (90)$$

$$NC\dot{S} + Ph\text{-}CH{=}CH\text{-}CH_2\text{-}Co(dmgH)_2Py \longrightarrow CH_2{=}CH\text{-}CH(Ph)(SCN) + \dot{C}o(dmgH)_2Py \quad (91)$$

$$NC\dot{S} + CH_2{=}CH\text{-}CH_2\text{-}Co(dmgH)_2Py \longrightarrow CH_2{=}CH\text{-}CH_2\text{-}SCN + Co(dmgH)_2Py \quad (92a)$$

$$NC\dot{S} + CH_2{=}CH\text{-}CH_2\text{-}Co(dmgH)_2Py \longrightarrow \text{cyclopropyl-}CH_2\text{-}NCS + Co(dmgH)_2Py \quad (92b)$$

$$(RCo(dmgH)_2Py) \longrightarrow \dot{R} + (Co(dmgH)_2Py) \quad (93)$$

$$\dot{R} + (SCN)_2 \longrightarrow RSCN + NC\dot{S} \quad (94)$$

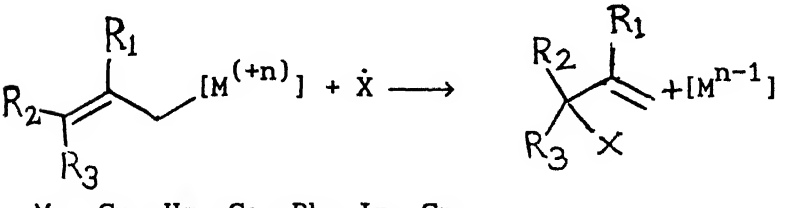
CHAPTER - 4

ORGANODICOBALOXIMES : HOMOLYTIC DISPLACEMENT AT A SATURATED CARBON CENTRE

CHAPTER - 4

4.1 BACKGROUND AND AIM OF THE STUDY :

The use of transition metal complexes in organic synthesis has seen considerable development in the past two decades. In these reactions, which can be stoichiometric or catalytic, the organic substrate are most often involved as π ligands which undergo electrophilic or nucleophilic attack by various reagents[121b]. Radical reactions of synthetic utility, by contrast, are scarce[239a-b]. However, after years of deliberations, organometallic compounds are now avowed to undergo free radical chain substitution (S_H2 or S_H2') reactions[240,320]. This is particularly so with organo-tin, mercury, chromium, cobalt, rhodium and iridium compounds[240,320] (eq. 95).



(95)

M = Sn, Hg, Co, Rh, Ir, Cr;

$\dot{X}$ = $\dot{C}XYZ$, $\dot{S}Ar$, $\dot{S}O_2Ar$, $\dot{S}O_2Me$, $\dot{S}ePh$, $\dot{S}Ph$, $ArSO_2\dot{N}Me$ etc.

However, little effort has been paid to exploit these reactions in formulating synthetically viable protocols towards useful organic intermediates. Among these, the organocobalt and organotin compounds have been used the maximum and the studies suggest a strong parallel between orgnotin and organocobalt chemistry. Surprisingly, the study is limited mainly to S_H2' reactions and the authentic examples of S_H2 reactions at a saturated carbon are

rather few[185,2391,f,321]. This is probably because the reactions are not clean and a mixture of products is generally formed in such reactions because of the participation of some ancillary processes[2391,321c].

$$ArCH_2\text{-}Co^{III} + RSO_2Cl \longrightarrow ArCH_2\text{-}SO_2R + ArCH_2\text{-}CH_2Ar + ArCH_2dmgH \quad (96)$$

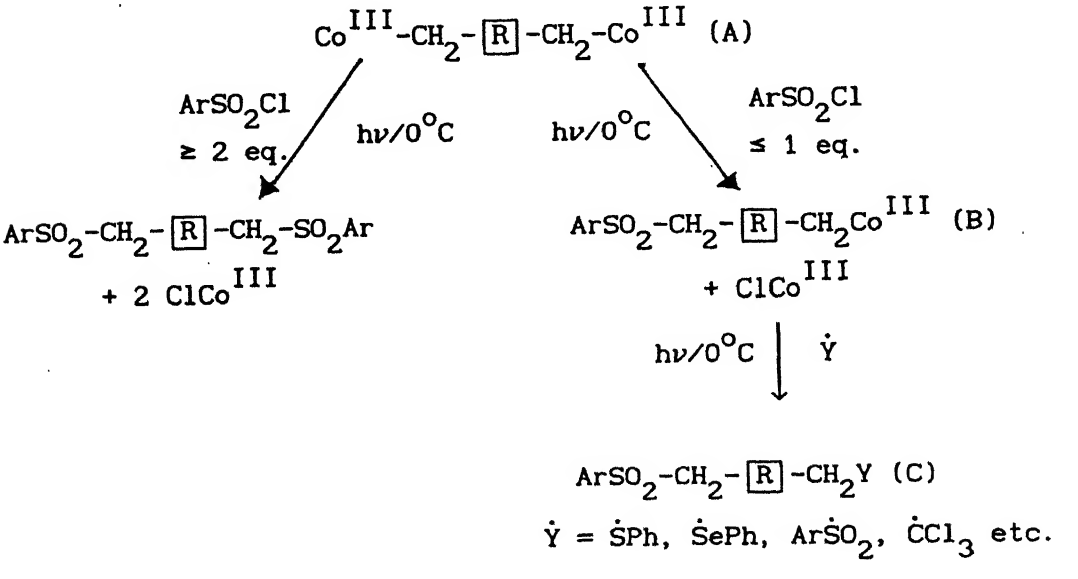
$$ArCH_2\text{-}Co^{III} + CCl_3SO_2Cl \longrightarrow ArCH_2CCl_3 + ArCH_2Cl + ArCH_2\text{-}CH_2\text{-}Ar \quad (97)$$

$$ArCH_2\text{-}Co^{III} + BrCCl_3 \longrightarrow ArCH_2CCl_3 + ArCH_2Br \quad (98)$$

Co = $Co(dmgH)_2Py$

The study, however, points to one very significant fact that organocobaloximes provide an excellent handle where the organic group can be functionalised by a variety of radicals. If one is able to eliminate these side reactions by designing suitable organocobaloximes, the study can provide synthetically useful routes and at the same time will also test the generality of these S_H2 reactions at a saturated carbon centre.

We have, therefore, taken up the study of the synthesis and reactions of organodicobaloximes with arene sulphonyl chlorides under photochemical conditions.



If we are able to form and isolate intermediate structures like (B), its further reactions with $\dot{Y}$ will lead to a variety of useful organic products (C).

4.2 Experimental

All reactions were carried out in oven dried apparatus. Reactions mixtures were stirred magnetically until otherwise mentioned. Reaction product solutions were concentrated at room temperature using either a Perfit rotary evaporator or a water aspirator.

The details of the solvents, gases, chromatography, physical measurements and instruments are same as those described earlier in Chapter 2, Sec. 2.2.

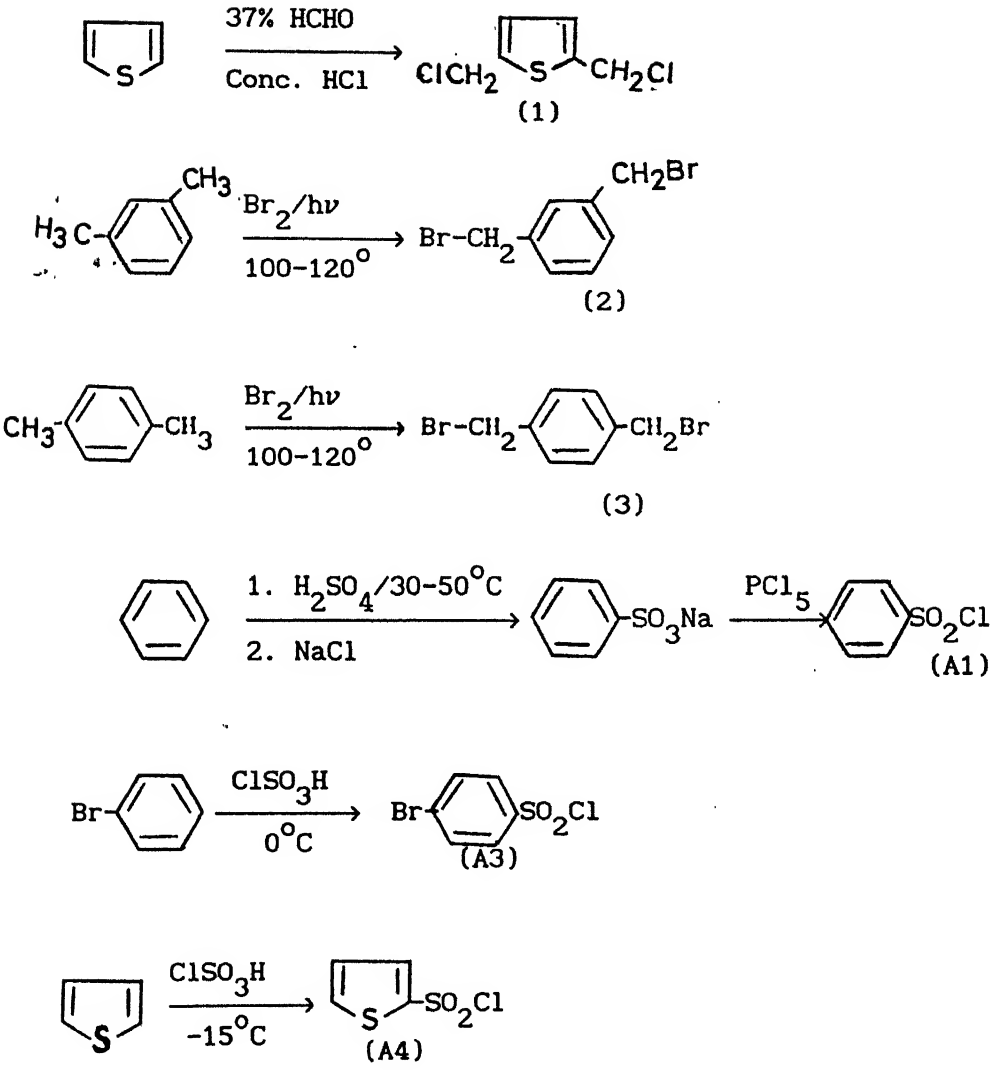
Starting Material and organocobaloximes

Bromine, meta and para xylene, thiophene, 1,4 dibromobutane, 37% formaldehyde solution, 4-toluene sulphonyl chloride were commercial materials and were used as such without any further purification.

4.2.1 Synthesis of organic precursors (1-3)

Preparation of bis (2,5 chloromethyl) thiophene[322] (1)

The title compound was prepared by the reaction of thiophene (6.97 g, 0.083 mol) with 37% formaldehyde solution (20.4 mL, 0.28 mol) and conc. HCl (5 ml) at 30°C. The usual work up followed by distillation gave bis (2,5 chloromethyl) thiophene (11.6 g, 78%) b.p. 108°C/5 mm (Lit[322] 106-108°C/5 mm). ^{1}H NMR (CCl_4) δ(ppm): 4.66 (s, CH_2), 6.86 (s, aromatic).


37% HCHO
Conc. HCl
ClCH2
CH2Cl
(1)
CH3
H3C
Br2/hν
100-120°
Br-CH2
CH2Br
(2)
CH3
CH3
Br2/hν
100-120°
Br-CH2
CH2Br
(3)
1. H2SO4/30-50°C
2. NaCl
SO3Na
PCl5
SO2Cl
(A1)
Br
ClSO3H
0°C
Br
SO2Cl
(A3)
ClSO3H
-15°C
S
SO2Cl
(A4)

Scheme 4.1

Preparation of meta xylylene dibromide[323] (2)

Meta xylylene dibromide was prepared from m-xylene (10.6 g, 0.1 mol) and bromine (35.2 g, 0.22 mol). Bromination was done at 100-120°C for 2h under photolytic conditions, yield (13.0 gm, 53%), m.p. 75-78°C (Lit.[323] 76°C). ^{1}H NMR ($CDCl_3$) δ(ppm) : 4.56 (s, CH_2), 7.30 (s, aromatic).

Preparation of para xylylene dibromide[323] (3)

Para xylylene dibromide was prepared by the bromination of p-xylene (10.6 g, 0.1 mol) with bromine under the identical conditions as described above, yield (14.9 gm, 60%), m.p. 140-141°C (Lit.[323] 141°C). ^{1}H NMR ($CDCl_3$) δ(ppm) : 4.5 (s, CH_2), 7.25 (s, aromatic).

4.2.2 Synthesis of organosulphonyl chlorides (A_1, A_3, A_4)

Preparation of benzene sulphonyl chloride (A_1)[324]

A mixture of sodium benzene sulphonate (9.0g) and powdered phosphorous pentachloride (5.0g) was heated at 170-180°C for 15h. The flask was thoroughly shaken every 3h duration after cooling. Finally the mixture was cooled and poured into crushed ice and extracted with carbon tetrachloride (2x15 ml). Removal of the solvent followed by distillation gave benzene sulphonyl chloride (A_1) (6.2g, 75%) b.p. 96°C/5 mm (Lit.[324] b.p. 118-120°C/15 mm). ^{1}H NMR (CCl_4) δ (ppm) : 7.66 (m); 8.06 (m).

Preparation of 4-bromobenzene sulphonyl chloride (A_3)[324]

Compound (A_3) was prepared by the above method by the reaction of bromo benzene (15.7 ml) with chlorosulphonic acid

(19.5 ml). The yield is 51%, m.p. 75°C. ^{1}H NMR (CCl_4) δ (ppm) : 7.88 (dd).

Preparation of Thiophene-2-sulphonyl Chloride (A_4)[325,326]

Thiophene (7.5g, 90 mmol) was added during 1h to stirred chlorosulphonic acid (30g, 175 mmol) at -15°C at such a rate that the temperature did not rise above -5°C. After addition of an equal volume of chloroform, the mixture was poured onto crushed ice, the chloroform layer was separated and washed with ice-cold water. After drying and removal of solvent it was distilled to give thiophene-2-sulphonyl chloride (A_4) (11.7g, 72%) b.p. 90°C/1 mm (Lit.[325] b.p. 94-98°C/1.5 mm). ^{1}H NMR (CCl_4) δ(ppm) : 7.20 (m); 7.93 (m).

4.2.3 Synthesis of Organodicobaloximes (4-7)

Organodicobaloximes (4-7) were synthesized following S.2 method as described in Chapter 2, Sec. 2.2 with the following modification.

Dihalide (1 mol) was reacted with $(Co^I)^-$ [3 mol] and the dicobaloxime so formed was washed thoroughly with water and then with solvent ether for cobaloxime (5-7) and with petroleum ether for cobaloxime (6) to remove excess of unreacted dihalide. We find that this procedure results in better yield than the reported synthesis[200b] for (4) and (5) where halide : $(Co^I)^-$ ratio taken was 1:2. Furthermore, we have found that the literature method always gave the organometallic product contaminated with the dihalide.

(4) Yield 71%; ^{1}H NMR ($CDCl_3$) δ(ppm) : 2.1 (s, 24H), 2.96 (s, 4H), 6.25-6.68 (m, aromatic), 7.22, 7.56, 8.3 [Pyridine, 10H] λ_{max} (MeOH) 390, 292, 241.

(5) Yield 70%; ^{1}H NMR ($CDCl_3$) δ(ppm) : 1.9 (s, 24H), 2.75 (s, 4H), 6.66-6.82 (m, aromatic), 7.24, 7.56, 8.46 [Pyridine, 10H] λ_{max} (MeOH) 411, 295, 238.

(6) Yield 68%; ^{1}H NMR ($CDCl_3$) δ(ppm) : 1.9 (s, 24H), 2.75 (s, 4H), 6.65 (m, aromatic), 7.26, 7.68, 8.5 [Pyridine, 10H]. λ_{max}(MeOH) 356, 284, 241.

(7) Yield 50%; ^{1}H NMR ($CDCl_3$) δ(ppm) : 2.1 (s, 24H), 3.3 (t, 4H), 0.8-1.9 (m, 4H), 7.35, 7.7, 8.6 [Pyridine, 10H] λ_{max} (MeOH) 446, 384, 290, 230.

All the organodicobaloximes (4-7) are fairly soluble in dichloromethane. Cobaloxime (5 and 6) are insoluble in diethyl ether but cobaloximes (4 and 7) are fairly soluble. In general, the organodicobaloximes are stored under dark. The R_f values of the organodicobaloximes is between 1-2 (on a 10-point scale) in ethyl acetate. This value is very low compared to its values for mono organocobaloximes which ranges between 4-5.

$$CoCl_2.6H_2O + 2\ dmgH_2 + Py$$
$$\downarrow 0^{\circ}(N_2)$$
$$[Co^{II}(dmgH)_2Py]_2$$
$$NaBH_4 \mid NaOH/N_2 \downarrow$$
$$[Co^{I}(dmgH)_2Py]^-$$
$$\mid R(CH_2X)_2 \downarrow$$
$$Py(dmgH)_2\ Co^{III}-CH_2-\boxed{R}-CH_2Co^{III}(dmgH)_2Py$$

(4-7)

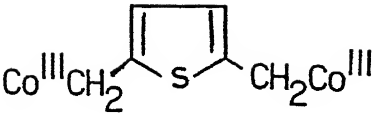
Scheme 4.2

4.3 Reaction of arene sulphonyl chloride with organodicobaloximes : General procedure

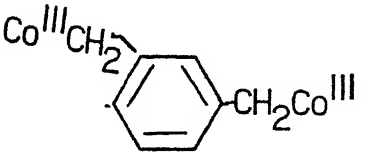
The reactions were carried out under photochemical conditions (P1 and P2).

Photochemical reaction using 2x200W tungsten lamps (method P1)

Pyridine (5 drops), organocobaloximes (1 mmol) and arene sulphonyl chloride (3 mmol) were added successively to degassed dichloromethane (25 mL). The solution was irradiated with 2x200W tungsten lamps kept at about 10 cm away from the reaction vessel while the temperature of the reaction was maintained at $0^{\circ}C$ by Julabo refrigerated circulator. On completion, the reaction was worked up by concentrating the solution in vacuo and was subjected directly to flash chromatography on silica gel using dichloromethane. The total organic product was separated out. The inorganic material was eluated out with ethyl acetate. The



(4)



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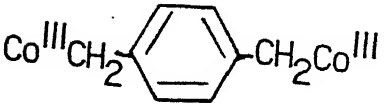

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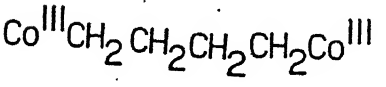


(7)

STRUCTURE OF ORGANODICOBALOXIME (4-7)

total organic product was loaded again on the silica gel gravity column and the eluent used were petroleum ether (60-80°C), petroleum ether: dichloromethane (1:1) followed by pure dichloromethane. The organic sulphones so obtained were characterised by conventional method.

Photochemical Reaction Using 400W Hg lamp (method P2)

Pyridine (5 drops), organodicobaloxime (1 mmol) and arene sulphonyl chloride (3 mmol) were added to degassed chloroform (25 mL). The solution was flushed with nitrogen for 15 min and was transferred to quartz tubes (15 mL capacity) under nitrogen. The tubes, after being stoppered, were irradiated in the photochemical reactor by a 400W mercury lamp placed inside the reactor while the temperature was maintained at 25°C by circulating cold water through the outer jacket of the photochemical reactor. On completion, the reaction mixture was worked up as described above under (P1) conditions.

4.4 Results

2,5 bis (thienyl methyl) dicobaloxime (4) reacts with arene sulphonyl chloride (A_1-A_4) in 1:3 molar ratio under photolytic condition (P1) and within 3h to give the corresponding monomethyl organic sulphone (8-11) in 60-92% yield. On the other hand, the corresponding reaction of 1,3 xylylene dicobaloxime (5) with (A_1-A_4) in 1:3 molar ratio under identical conditions form the disulphones (12-15) in only (10-25%) yield. Similarly (6) and (7) with (A_2) forms the corresponding sulphones (16 and 17). The details of the organic products and their characteristics are described in Scheme 4.3 and table 4.1.

The following independent experiments were performed to characterise the reaction further.

a) The change of solvent does not change the nature and yield of the reaction, for example (4) with (A_2) in benzene forms (9) in 80% yield. However, the reaction was slower (6h) as compared to the identical reaction in dichloromethane.

b) In general, the reactions carried out in molar ratios less than 1:3 (dicobaloxime:reagent) remain incomplete and tend to form side products in addition to the required major product.

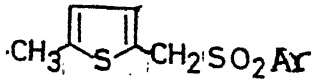
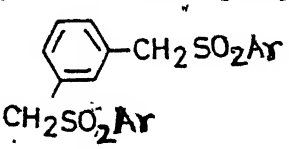
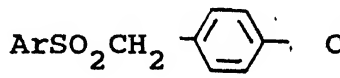
c) The reactions are inhibited by radical traps like galvinoxyl and are accelerated by cobaloxime(II) or benzoyl peroxide (5% w/w).

d) In the blank experiments, all the organodicobaloximes are stable under the reaction conditions and no decomposition of any kind takes place.

e) The reactions are faster in P2. However, the yield is low compared to the identical reactions under P1.

$Co^{III}CH_2$-[R]-CH_2Co^{III} + $ArSO_2Cl$ $\xrightarrow{P_1}$ Organic Products + $ClCo^{III}$

(4-7) (A_1-A_4) (8-17) (24)

Organodicobaloximes	$ArSO_2Cl$	Products [yield[a,b] %]
(4)	(A_1-A_4)	
		(8) Ar = Ph [60]
		(9) = 4-MeC_6H_4 [75]
		(10) = 4-BrC_6H_4 [62]
		(11) = Th[c] [92]
(5)	(A_1-A_4)	
		(12) Ar = Ph [25]
		(13) = 4-MeC_6H_4 [20]
		(14) = 4-BrC_6H_4 [10]
		(15) = Th[c] [22]
(6)	A_2	
		(16) Ar = 4-MeC_6H_4 (18)
(7)	A_2	$CH_3CH_2(CH_2)_2CH_2SO_2Ar$
		(17) Ar = 4-MeC_6H_4 (15)

a) Isolated yield after chromatographic separation.

b) Reaction conditions : P1/0°C/CH_2Cl_2/3h ; Molar ratio organodicobaloxime : $ArSO_2Cl$ (1:3).

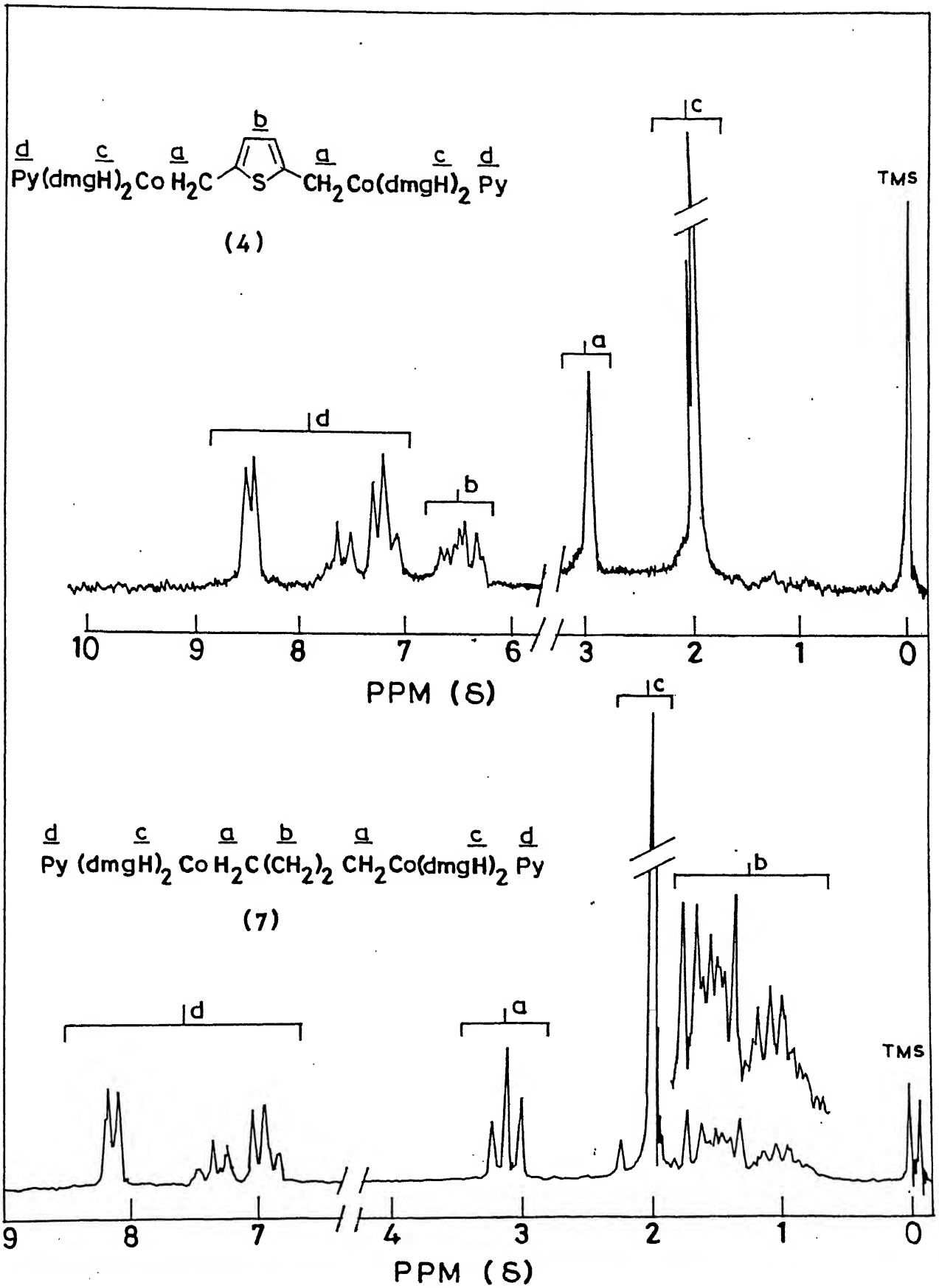
c) Th = 2-Thiophene

Scheme 4.3

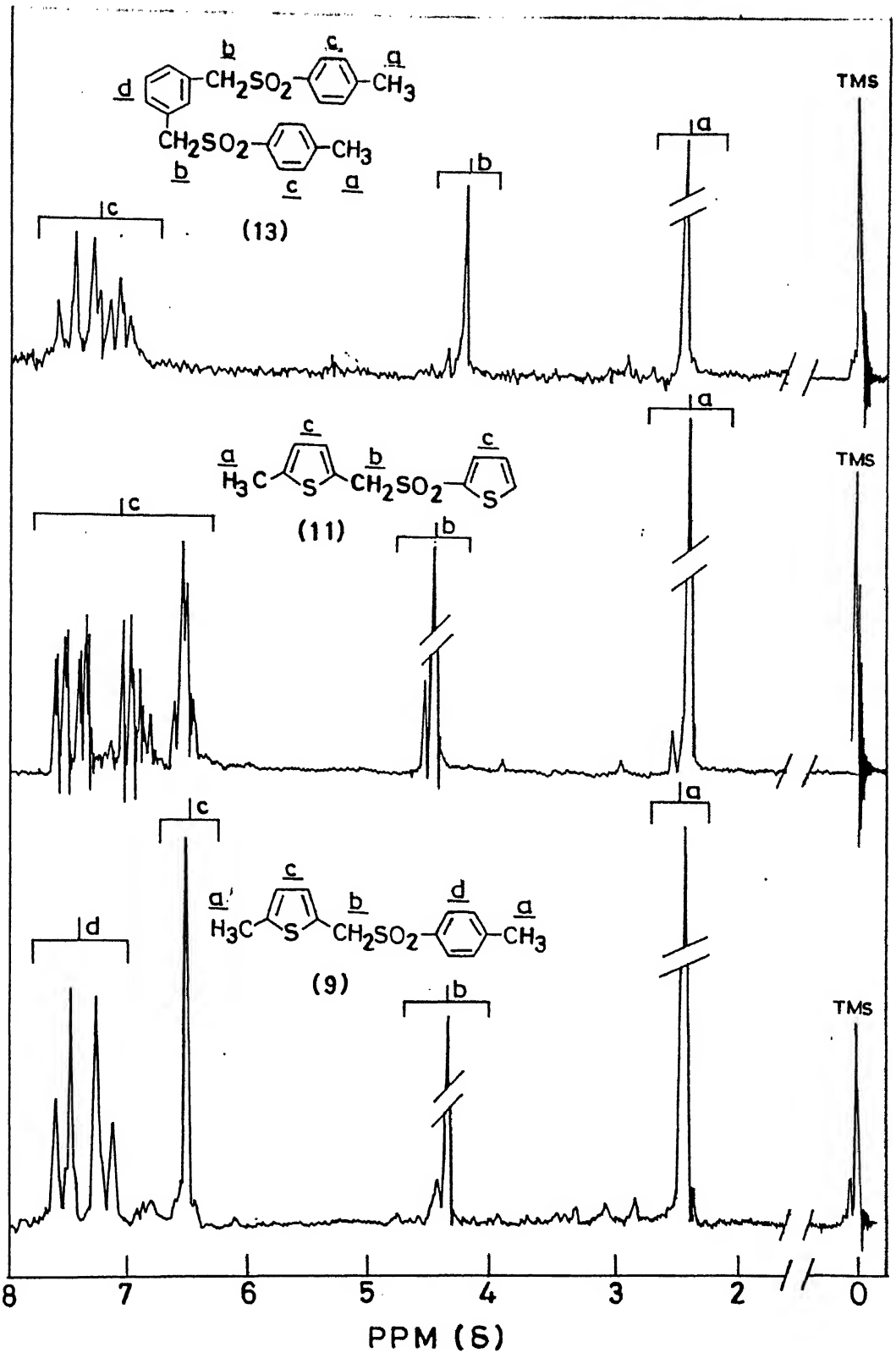
Table 4 - 1 Characteristics of Organic products (8-17)

Product No.	^{1}H NMR (δ) ppm (multiplicity) $-CH_2$	Aromatic	Others	UV-VIS λ_{max}(nm) (CH_3OH)	M.P. (0^oC)
(8)	4.3 (s)	6.5 (s), 7.36-7.7 (m)	-	236, 238	110
(9)	4.36 (s)	6.5 (s), 7.1-7.6 (dd)	-	238, 242	135
(10)	4.4 (s)	6.56(s), 7.56 (s)	-	237	140
(11)	4.4 (s)	6.56 (s), 6.9-7.7 (m)	-	240	88
(12)	4.2 (s)	7.0 (m), 7.6 (m)	-	255, 268	210[d]
(13)	4.24 (s)	7.0-7.57 (m)	2.42 (s)	260, 271	240[d]
(14)	4.28 (s)	7.35 (s), 7.7 (dd)	-	258, 270	200[d]
(15)	4.31 (s)	7.0-7.7 (m)	-	258, 271	164[d]
(16)	4.18 (s)	7.0-7.7 (m)	2.4 (s)	225, 261	220[d]
(17)	3.35 (t)	7.06-7.66 (m)	1.6-2.66 (m)	224, 262	viscous

d = decomposition temperature



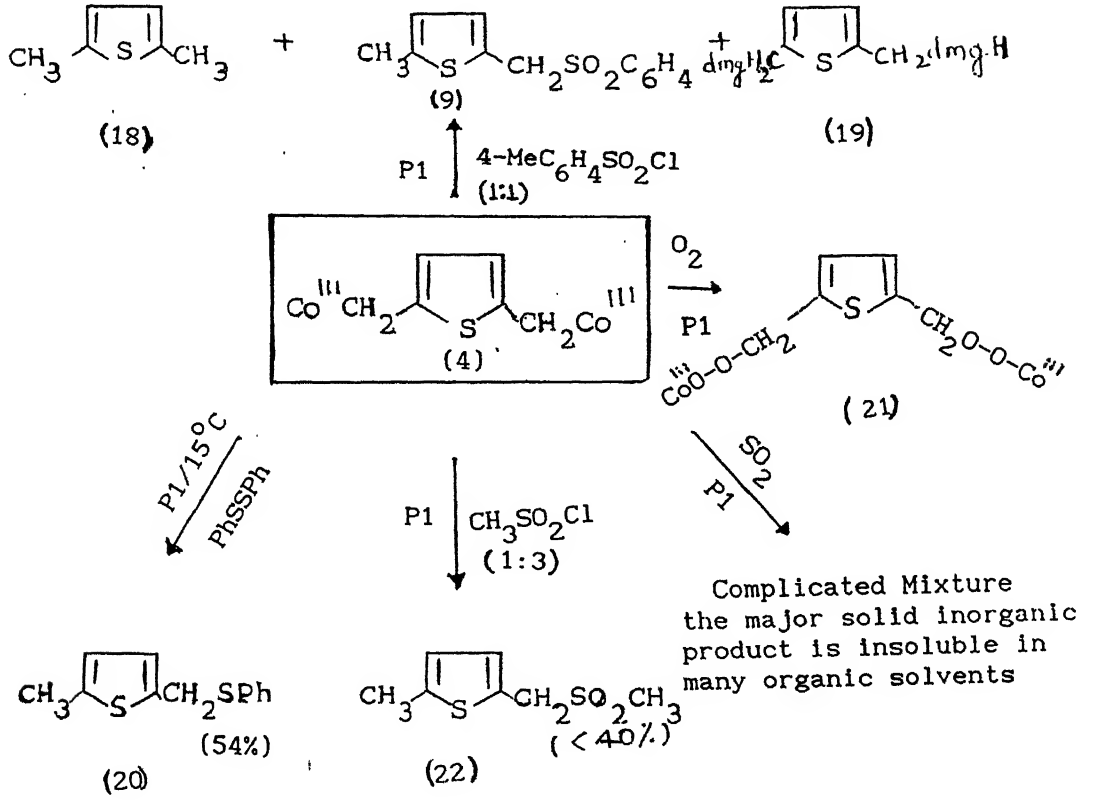
^1H NMR SPECTRA (60 MHz) OF (4) & (7).



^1H NMR SPECTRA (60MHz) OF (13), (11) & (9).

4.4.1 Miscellaneous reactions :

In addition, many miscellaneous reactions with 2,5 bis-(thienylmethyl) dicobaloxime (4) were done and are described in scheme 4.4.



Scheme 4.4

^{1}H NMR and UV of products (18-22)

(18) ^{1}H NMR (CCl_4) δ(ppm) : 2.4 (s, 6H), 6.6 (s, aromatic), λ_{max} (MeOH) : 234.

(19) ^{1}H NMR (CCl_4) δ(ppm) : 2.0 (m, 12H), 5.1 (s, 4H), 6.6 (m, 2H).

(20) ^{1}H NMR (CCl_4) δ(ppm) : 3.34 (s, 3H), 4.06 (s, 2H), 6.26-6.5 (m, 2H), 7.0 (m, 5H), λ_{max} (MeOH) : 254, 208.

(21) ^{1}H NMR (CCl_4) δ(ppm) : 2.13 (s, 12H), 3.7 (s, 2H), 6.24-6.7 (m, 2H), [7.13-7.4, 7.7, 8.5] (m, 5H).

(22) ^{1}H NMR (CCl_4) δ(ppm) : 2.7 (s, 3H), 2.8 (s, 3H), 4.3 (s, 2H) 6.6-6.8 (dd, 2H), λ_{max} (MeOH) : 296, 236.

4.5 Discussion

All the reactions described in this chapter are free radical in nature. Although the evidence is indirect, it is certain that free radical abound under all the condition described. The cleavage of Co-C bond is a key feature of these reactions and therefore needs to be examined. It is well established that homolysis of the Co-C bond in organocobaloximes takes place very readily even on irradiation at wave lengths greater than 360 nm[234b,235,327]. This is consistent with the low Co-C bond energy 17-25 KCal mol^{-1} in such substrates[43,53a,135,134a]. The low value of the Co-C bond energy and its high valent nature suggest that it is much weaker compared to other M-C bonds and is susceptible to homolytic cleavage which may even be affected by visible radiation. Tungsten lamps and glass apparatus are, therefore, adequate for any photolytic experiment. Cobaloxime(II) a d^7 species, formed on homolysis of the Co-C bond, has been shown to be a good leaving group in many such similar

studies[86,187,239e,h,j,241]. Unlike the conventional organic free radicals, it can be easily prepared and can be stored in inert atmosphere indefinitely. It neither disproportionates nor dimerises in neutral solvents. Organosulphonyl chlorides, $ArSO_2Cl$, have been identified as chain propagating species in many organic reactions of alkenes and its potential as a free radical precursors is well established in the literature[328]. Also, the reaction of cobaloxime(II) with tosyl chloride gives good yield of chlorocobaloxime and tosylcobaloxime.

The results presented in this chapter are only preliminary and we believe that it is very difficult to draw any final conclusions before some more studies is done. However, the preliminary results are very significant and the following points emerge from the study.

1. The formation of disulphone (12-16) in cobaloximes (5 and 6) and monomethyl sulphones (8-11) and (17) in cobaloximes (4 and 7) suggests that their mechanism of formation is different in these two cases.

In view of the nature of products and the influence of initiator and inhibitors on the rates of reaction which point to the free radical nature of these reactions, it is likely that the mechanism is similar to the one proposed by us for the formation of benzyl sulphones from benzyl cobaloximes and $ArSO_2Cl$[239i]. The low yield of disulphones, however, suggests that some ancillary processes are also operating and the formation of disulphones by a coupling process can not be ruled out at this stage.

It is certainly clear that the hydrogen required in the formation of monomethylsulphone does not come from the solvent. It is likely that such a product may arise by an initial attack of the $Ar\dot{S}O_2$ radical on cobalt forming a transient organocobalt(IV) species, followed by homolysis of Co^{IV}-C bond with a simultaneous abstraction of the hydrogen from the equatorial ligand. Such a mechanism has been proposed earlier for the hydrocarbon formation in the reactions of allenyl cobaloximes with $BrCCl_3$[184]. This viewpoint however needs confirmation by more experiments. However, it is worth noting that such similar organocobalt(IV) complexes have been described in literature and are known to undergo homolysis under these reaction conditions[239i,184,256]. The formation of 2,5 dimethyl thiophene (18) and 2-thienylmethyl glyoxime ether (19) in the reaction of (4) with (A_2) in 1:1 molar ratio lends indirect support to the above viewpoint. Similar ether products are known to be formed as the characteristic decomposition products of organocobalt(IV) species in solution[213,329].

2. The low yield of disulphones in (5) and (6) is probably because of the high tendency of the benzylic radicals to dimerisation. This is supported by the fact that reactions of (6) with (A_2) forms a very hard material which has very little solubility in solvents like chloroform, methanol, ether and is sparingly soluble in dichloromethane.

3. The electrophilicity of the sulphur radical seems to play an important part in these reactions, for example, the reaction of (4) with $\dot{S}Ph$ and $CH_3\dot{S}O_2$ radical give poor yield of organo sulphur products (see results in Scheme 4.3).

4. The Co-C bond in the dicobaloximes readily undergoes insertion by oxygen just like the organocobaloximes, but the SO_2 insertion is very messy and no inserted product is formed. This is in contrast to very clean reactions of organocobaloximes with SO_2[331].

5. All efforts to obtain the intermediate $ArSO_2CH_2-\boxed{R}-CH_2Co^{III}$ have failed.

6. In general, the reactions are much faster under P2 conditions.

CONCLUSION AND SCOPE FOR FUTURE WORK

The Chemistry of Organocobalt(III) complexes has gained a wider perspective and tremendous amount of work has already been done on these complexes, primarily with an aim to understand the chemistry of B_{12} coenzyme catalyzed reactions. The study presented in this dissertation clearly shows that, with the same reagent Arene sulphenyl chloride the organocobaloximes exhibit different reactionpathways. The alkyl and benzyl cobaloximes undergo bimolecular homolytic displacement reaction with the electron transfer process occuring in the later as a competitive process. The reactions of heteroaromatic methyl cobaloximes are quite complex in nature because of the simultaneous participation of a number of reaction processes. The preference of one process over the other is guided by many factors like the nature of the substrate cobaloxime, arene sulphenyl chloride and the reaction conditions. Therefore, it becomes a very difficult task to precisely estimate the relative contribution of each of these processes. To understand it better a greater variety of electrophiles under diverse conditions need to be investigated. Furthermore, accurate kinetic studies are necessary to prove conclusively the reaction pathway.

It is now well established that the Co-C bond in organocobaloximes can be easily functionalised by free radical precursors, the synthesis of organodicobaloximes having two Co-C centre has opened an area for the synthesis of a wide variety of organic products. Further work in this direction is warranted.

Since Organocobaloximes have been used as catalysts in many reactions, new optically active cobaloximes need to be synthesized with an aim that they may provide new information on the elementary process of catalytic reactions, especially catalytic asymmetric reactions.

Free radical Carbon-Carbon bond forming reactions have gained a tremendous attention recently. The use of carbon radicals in the elaboration of carbo- and heterocyclic molecules is particularly illustrative, and has provided new dimensions in this important area. The versatility of radical initiated Carbon-Carbon bond forming reactions will enhance still further if practical procedures are designed to introduce functionality in consult with C-C bond formation, using appropriate radical trapping agents.

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V I T A É

Born on June 8, 1965 at Dehradun, Uttar Pradesh, the author had her earlier education at Central School. She took her B.Sc. degree in 1985 and M.Sc. degree in 1987 at Department of Chemistry, University of Kanpur. She joined the Ph.D programme of the Department of Chemistry, **IIT,KANPUR** in December 1988 and is presently continuing as a **Senior Research Scholar** in the same department.